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Studies of the Direct Dissolution of Metal in a β-Diketone Reagent[*1]

Kimitaka SATO and Ohiko KAMMORI

Tokyo Research Institute, Yawata Iron and Steel Co., Ltd., Ida, Kawasaki

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As it was found that metallic iron is dissolved in acetylacetone (Hacac), the interaction between the solute and the solvent in the dissolution phenomena, together with the process of the dissolution of metal, were examined in detail in order to apply it to analytical techniques. The factors of the oxygen, the co-existing water, and the dissociated proton in acetylacetone were shown to be effective in the dissolution. With typical β-diketones, the exception of acetylacetone, such as trifluoroacetylacetone (HTFA), hexafluoroacetylacetone (HHFA), benzoyltrifluoroacetone (HBTA), 2-furoyltrifluoroacetone (HFTA), and 2-thenoyltrifluoroacetone (HTTA), were also employed; they were shown to have the same properties as the above one. The relationship between the solubilities of metals and the effect of adding an organic solvent, the equilibrium reactions of fluorine-containing β-diketones with water or alcohols, or the preferred enol forms of trifluorosubstituted β-diketones, were also discussed, paying attention to the accelerating effects of the solvents on the dissolution.

In general, water is employed as the solvent in the chemical analysis of iron and steel. Sometimes, however, troubles rise because of the use of an aqueous solution; for example, sometimes minute extracts float on the liquid surface in the case of separation by a centrifuge in electro-analysis. It is necessary to utilize an organic solvent effectively in solving the difficult points, so a method of electrolysis in non-aqueous solution has already been attempted.[1)]

Since β-diketone was found, in fundamental studies of the production of ultrapure iron by means of an organochemical technique in our laboratory,[2)] to have the property of dissolving metals, the present investigation was undertaken to apply the dissolution phenomena to the analysis of iron and steel. It is possible to apply the phenomena extensively to various fields of analysis. Thus, it is expected that new, simple analytical techniques can be developed by using, together with chemical analysis, gas chromatography, polarography, *etc.*[3,4)] For the above-mentioned reasons, basic problems in the phenomena were studied in detail from the point of view of analytical chemistry.

β-Diketone is well known to have the following keto-enol tautomerism[5–10)] (Eqs. (1) and (2)). Consequently, the dissociated proton is expected to have some effect on the dissolution of metal in β-diketone, as in the case of inorganic acids. On the other hand, Charles and Barnartt[11,12)] studied

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[*1] A part of this study was presented: a) by O. Kammori, K. Sato, K. Takimoto and K. Arakawa at the 14th Annual Meeting of the Japan Society for Analytical Chemistry, Kyoto, November, 1965; b) by O. Kammori, K. Sato, K. Takimoto and K. Arakawa, *Japan Analyst*, **15**, 561 (1966); c) by O. Kammori, N. Yamaguchi and K. Sato, *ibid.*, **15**, 1043 (1966); d) by K. Sato, Y. Kodama and K. Arakawa, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **87**, 821 (1966); e) by Y. Kodama, K. Sato and K. Arakawa, *ibid.*, **87**, 1092 (1966); f) by K. Sato and K. Arakawa, *ibid.*, **88**, 470 (1967); g) by K. Sato, Y. Kodama and K. Arakawa, *ibid.*, **88**, 968 (1967); h) by K. Sato, H. Ochi and K. Arakawa, This Bulletin, **42**, 1747 (1969), and i) by K. Sato and K. Arakawa, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **89**, 1110 (1968).

1) a) O. Kammori, I. Taguchi and A. Ono, *J. Japan Inst. Metals*, **32**, 55 (1968). b) O. Kammori, I. Taguchi, K. Suzuki and A. Ono, *ibid.*, **32**, 629, 1183 (1968).

2) K. Arakawa, *Nippon Butsuri Gakkaishi (Tokyo)*, **21**, 523 (1966) (in Japanese).

3) O. Kammori, K. Sato, K. Takimoto and K. Arakawa, *Japan Analyst*, **15**, 561 (1966).

4) O. Kammori, N. Yamaguchi and K. Sato, *ibid.*, **15**, 1043 (1966).

5) J. D. Park, H. A. Brown and J. R. Lacher, *J. Am. Chem. Soc.*, **75**, 4753 (1953).

6) R. L. Belford, A. E. Martell and M. Calvin, *J. Inorg. Nucl. Chem.*, **2**, 11 (1956).

7) J. L. Burdett and M. T. Rogers, *J. Am. Chem. Soc.*, **86**, 2105 (1964).

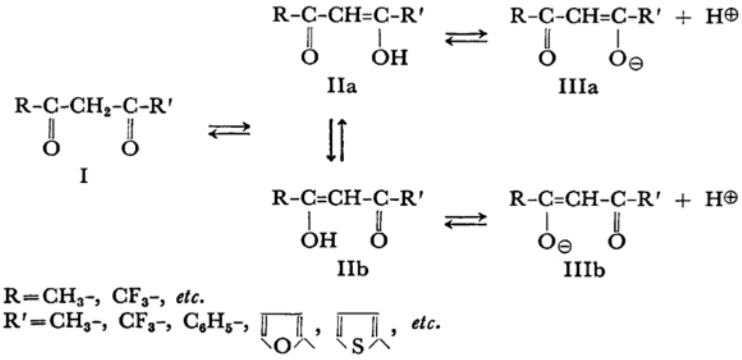
8) K. Kondo, Y. Kondo, T. Takemoto and T. Ikegami, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **68**, 1404 (1965).

9) Y. Kodama, K. Sato and K. Arakawa, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **87**, 1092 (1966).

10) K. Sato and K. Arakawa, *ibid.*, **89**, 1110 (1968).

11) R. G. Charles and S. Barnartt, *J. Phys. Chem.*, **62**, 315 (1958).

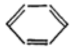
12) S. Barnartt, R. G. Charles and L. W. Littan, *ibid.*, **62**, 763 (1958).



(1)

(2)

TABLE 1. STRUCTURES AND PHYSICAL PROPERTIES OF SIX β-DIKETONE REAGENTS ($R\cdot CO\cdot CH_2\cdot COR'$)

β-Diketone	Symbol	R	R'	Physical constant	
				mp	bp
Acetylacetone	Hacac	CH_3	CH_3	−23.2°C	137—140°C
Trifluoroacetylacetone	HTFA	CH_3	CF_3	—	107°C
Hexafluoroacetylacetone	HHFA	CF_3	CF_3	—	70.0—70.2°C
2-Furoyltrifluoroacetone	HFTA		CF_3	19—20°C	89—90°C (14 mmHg)
2-Thenoyltrifluoroacetone	HTTA		CF_3	42.5—43.5°C	103—104°C (9 mmHg)
Benzoyltrifluoroacetone	HBTA		CF_3	39—41°C	224°C

the rate theory in the reaction by concentration on the effect of oxygen in the dissolution of metals in acetylacetone. It is presumed, however, that there are other important factors in the dissolution phenomena, but the general properties have never been established in detail.

In the present paper, we will present the detailed results of an investigation made of the phenomena and the related reactivities as well as of the characteristics of β-diketone.

Experimental

Materials. The β-diketones employed are listed in Table 1. The acetylacetone was a commercial product and was also purified by distillation under reduced pressure. Hexafluoroacetylacetone obtained from the Pierce Chemical Company (U.S.A.) and the other β-diketones were used without further purification. The organic solvents and $Fe(acac)_3$ were commercially-available products of sufficient purity.

The metals were all extra-pure, commercially-available products. The metals, aluminum, beryllium, copper, manganese, molybdenum, nickel, lead, silicon, titanium, tungsten, and zinc, were sheets in shape, while the specimens of calcium and iron were granular, those of cerium, cobalt, and chromium were massive, and that of magnesium was coil-like.

Measurements. *The UV and Visible Spectra* were taken with a Cary model 14 recording spectrometer. A quartz absorption cell, 10 mm long, was used, but the measurements of absorbance in the experiment of dissolution were carried out with a Tokyo-Koden model ANA-7E colorimeter, using a glass cell of 20 mm long.

The NMR Spectra were measured at room temperature with a JNM C-60 high-resolution nuclear magnetic resonance spectrometer, using as the internal standards tetramethylsilane (TMS) in proton resonance and monofluorotrichloromethane in fluorine resonance.

Gas Chromatography was performed with a Perkin-Elmer 154 vapor fractrometer by using a column of Carbowax 1500/chromosorb W, with helium as the carrier gas.

The gas evolved in the dissolution was confirmed with a CEC 21-103C mass spectrometer.

Effective Factors in the Dissolution

When acetylacetone (Hacac) was left alone on the steel plate, a part of the iron is dissolved and red crystals appear. In order to explain the dissolution phenomena, external factors in the dissolution system and the chemical properties inside the system must be taken into consideration. We have already cited as the factors: 1) the proton dissociated in the β-diketone molecule, 2) the co-existing water in β-diketone, and 3) the oxygen dissolved in β-diketone.[3)]

Effect of Proton Dissociated in β-Diketone Molecule. β-Diketone exists as an equilibrium mixture of keto-enol tautomers. The NMR method is most favorable for determining the enol

TABLE 2. KETO-ENOL RATIO OF THE ACETYLACETONE INVOLVING WATER

Condition	Method employed	Keto form (%)	Enol form (%)	Reference
Hacac only	PMR[a]	16	84	Kammori *et al.*[c]
	PMR	15	85	Jarrett *et al.*[d]
	PMR	24	76	Bhar[e]
	PMR	18.6	81.4	Reeves *et al.*[f]
	BT[b]	24	76	Meyer *et al.*[g]
Water-saturated Hacac	PMR	19	81	Kammori *et al.*[c]
A little Hacac in water	PMR	81	19	Kammori *et al.*[c]

a) Proton magnetic resonance.
b) Bromide Titration.
c) Ref. 3.
d) H. S. Jarrett, M. S. Sadler and J. N. Shoolery, *J. Chem. Phys.*, **21**, 2092 (1953).
e) B. N. Bhar, *Arkiv. Kemi*, **10**, 223 (1956).
f) Ref. 13.
g) K. Meyer *et. al.*, *Ber.*, **44**, 2718 (1911); **45**, 2843 (1912); **47**, 826, 832 (1914).

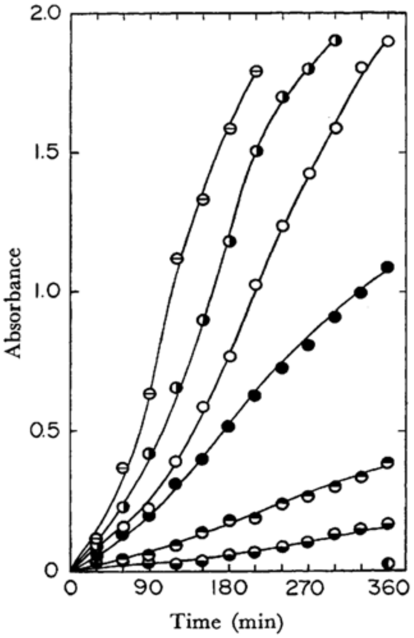


Fig. 1. Variation of solubility of iron in HTTA-methanol solution according to its concentration of HTTA.

◐, 0.0172 mol ◒, 0.0344 mol
◓, 0.0689 mol ●, 0.1379 mol
○, 0.2068 mol ◑, 0.2758 mol
⊖, 0.3448 mol (Fe: 2.0 mg)

Conditions:
Solution, 10 m*l*
Reference, methanol
Cell, glass with 20 mm long
Wavelength, 500 mμ

ratio, which was found to be 81.4% in Hacac[13] and 100% in HTFA or HHFA.[14] Moreover, the degree of the dissociation of the proton in enolized β-diketone is appraised as the acid strength, pK_a, the values of which are, respectively, 9.7 and 6.7 in Hacac and HTFA.[15] Therefore, the proton is regarded as taking part in the dissolution as in the decomposition of metal by hydrochloric acid and sulfuric acid. The keto-enol ratio of β-diketone also changes according to the kind of solvent[16] and according to the ratio of mixing with water, as is shown in Table 2.

The metals are more or less readily dissolved in solutions containing β-diketone in a greater enol ratio, but it is hard to dissolve them in a solution of β-diketone with a smaller enol ratio. The tendency of the metallic iron to dissolve was examined in HTTA-methanol solutions with different contents of HTTA, as is shown in Fig. 1. Iron is dissolved well as the concentration becomes larger. It may be concluded from the results that the proton contributes effectively to the dissolution.

Effect of Oxygen Dissolved in β-Diketone. Oxygen may be considerably dissolved in liquid β-diketone. Though the solubility of oxygen in water and typical organic solvents has already been measured, the solubility for liquid β-diketone has never been measured; however, it may be estimated to be equal to that for acetone, which is about ten times more than that of water.[17]

On the effect of oxygen, Charles and Barnartt[11] have already studied it in relation to the catalytical reaction. We investigated the same problem in

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[13] L. W. Reeves, *Can. J. Chem.*, **35**, 1351 (1957).

[14] J. D. Park, H. A. Brown and J. R. Lacher, *J. Am. Chem. Soc.*, **75**, 4753 (1953).

[15] A. E. Martell and M. Calvin, "Chemistry of the Metal Chelate Compounds," Prentice-Hall, Englewood Cliffs, N. J. (1956), p. 152.

[16] J. A. Pople, W. G. Schneider and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., New York, Tronto, London (1959), p. 436; *cf.* also Ref. 13.

[17] The Chemical Society of Japan, ed., "Kagaku Binran (New Edition)," Maruzen, Tokyo (1958), pp. 571, 576.

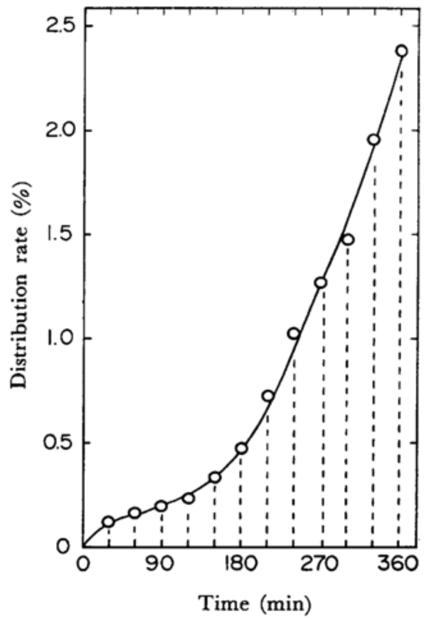

Fig. 2. Effect of oxygen on the solvency of iron in commercial acetylacetone by photometric determination.
○, Commercial Hacac (Fe: 1.700 mg)
Iron (1.787 mg) was not dissolved in deoxidated commercial Hacac for 360 min.

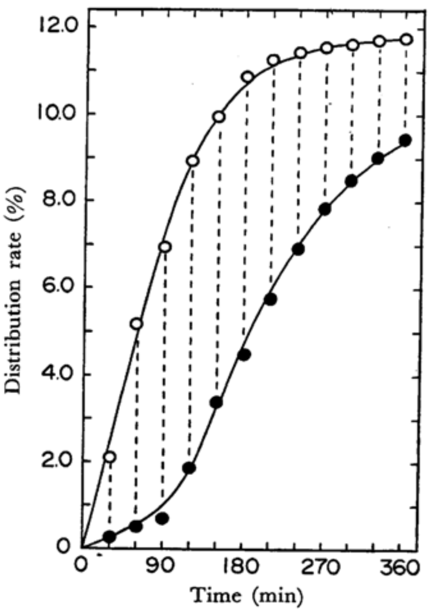

Fig. 3. Effect of oxygen on the solvency of iron in Hacac (10 ml) - H_2O (0.1 ml).
○, Hacac (10 ml) - H_2O (0.1 ml) (Fe: 1.582 mg)
●, Deoxidated (Fe: 1.660 mg)

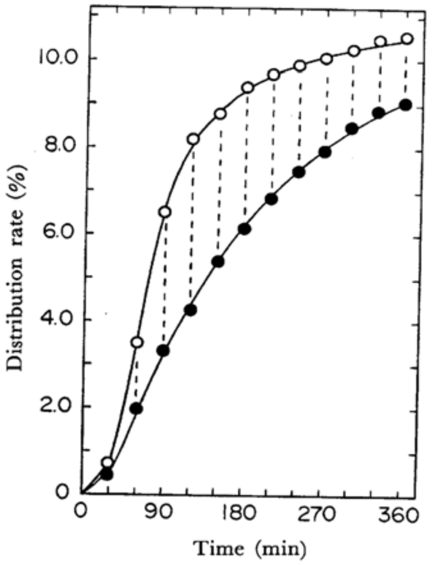

Fig. 4. Effect of oxygen on the solvency of iron in Hacac (10 ml) - H_2O (1 ml).
○, Hacac (10 ml) - H_2O (1 ml) (Fe: 1.740 mg)
●, Deoxidated (Fe: 1.596 mg)

detail from the point of view of analytical application. It was confirmed qualitatively, by the Winkler method, that considerable oxygen is dissolved in Hacac. Oxygen in 10 ml of liquid is removed, to the extent that no more could be detected by polarographic waves, by blowing nitrogen gas into the liquid for about 20 min. Accordingly, the effect of oxygen was investigated by blowing nitrogen gas into the solution for 30 min in order to compare the solvency of iron in the absence and presence of oxygen. Figure 2 shows the effect of oxygen in the dissolution of iron in commercial Hacac, which is expressed as the dotted line. The effects of oxygen in the case of adding 0.1 and 1.0 ml of water to the Hacac are shown in Figs. 3 and 4 respectively. The effect was found to become somewhat smaller when a lot of water was added. These results clearly show that oxygen is one of the important factors in the phenomena. Since it was observed that the solubility of iron increases with the quantity of water added to Hacac, as will be discussed later, the effect was further examined by adding ammonium persulfide, which acted effectively in oxidation. The correlation between the ammonium persulfide content and the dissolving time of iron obtained is shown in Fig. 5. The addition of ammonium persulfide was easily found to be more effective. Ammonium persulfide is dissolved into water as follows (Eq. (3)):

$$(NH_4)_2S_2O_8 + H_2O \rightleftarrows (NH_4)_2SO_4 + H_2SO_4 + (O) \qquad (3)$$

Consequently, a lot of nascent oxygen may occur and play an effective role, together with sulfuric acid, in the dissolution of iron.

Effect of Co-existing Water in β-Diketone.

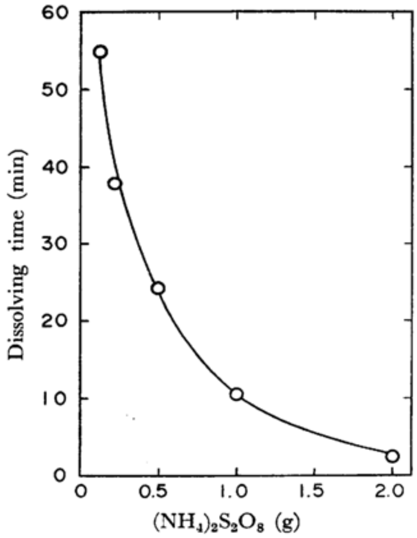

Fig. 5. Effect of addition of ammonium persulfide.
Conditions: Hacac, 10 m*l*; H_2O, 10 m*l*; Fe, 1 mg

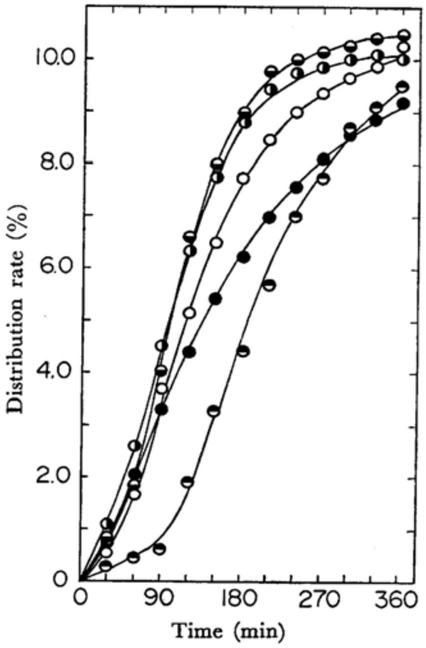

Fig. 6. Effect of water on the solvency of iron in Hacac.
Water contents in 10 m*l* of Hacac:
◓, 0.1 m*l* ◒, 0.3 m*l*
○, 0.5 m*l* ◑, 0.7 m*l*
●, 1.0 m*l* (Fe: 1.5—2.0 mg)

Since a little water is dissolved at the same time in liquid *β*-diketone, the influence of water on the dissolution of metal was also studied. The values of the water content in Hacac are listed in Table 3 along with those of the ratio of the area obtained in gas chromatography. A trace of water which could not easily be removed was found to be present

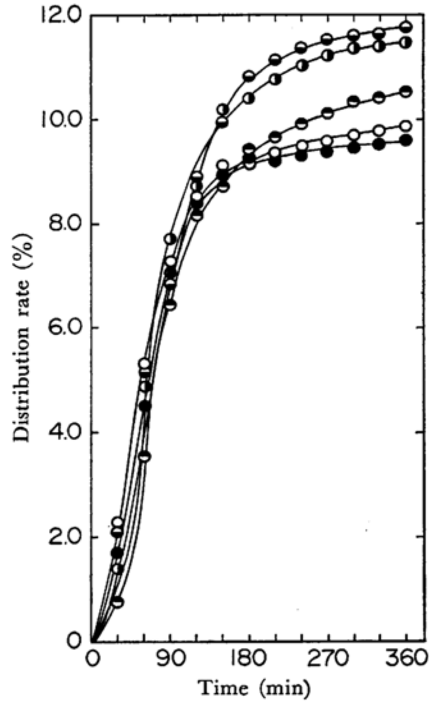

Fig. 7. Effect of water on the solvency of iron in Hacac, which is not deoxidated.
Water contents in 10 m*l* of Hacac:
◑, 0.02 m*l* ●, 0.04 m*l*
◒, 0.1 m*l* ○, 0.5 m*l*
◓, 1.0 m*l* (Fe: 1.5—2.0 mg)

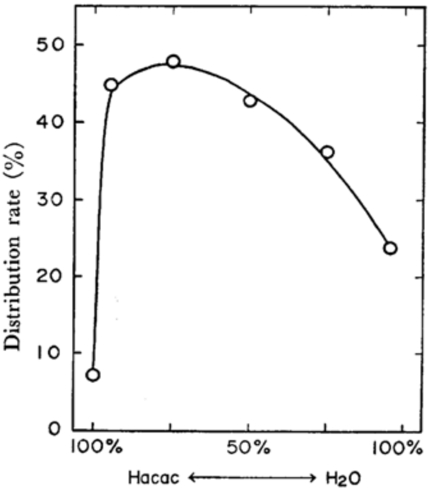

Fig. 8. Correlation between solvency of iron and Hacac-H_2O ratio.
Conditions:
Total volume of Hacac and H_2O, 20 m*l*
Fe, 1—2 mg
Treating time, 100 min

in the Hacac. The dissolution curve in Fig. 6 shows that only the co-exsisting water is clearly effective, even in the case of Hacac in the absence of oxygen.

TABLE 3. DETERMINATION OF WATER IN ACETYLACETONE

Condition	H_2O/Hacac	H_2O in Hacac 10 ml (μl)
Commercial	1/1500	6.86
Purified	1/4800	2.08
Purified	1/8000	1.25

The tendency toward much greater solvency upon the addition of water was further examined. Figure 7 shows an example of the experimental results regarding the effect of the solvency of iron in Hacac containing 0.02—1.0 m*l* of water. Water, 0.04 m*l*, is dissolved completely into 10 m*l* of Hacac, but when there is more than 0.05 m*l* of water the solution is separated into two layers. In terms of solubility, the metal was found to be dissolved effectively in such a solution. Figure 8 shows the solvency of iron in a solution containing Hacac and water, the total quantity of which is definite. The solvency was found to be best in a solution consisting of Hacac : water=3 : 1 (vol.).

Phenomena of Dissolution

Solubilities of Various Kinds of Metals in Acetylacetone. The solubilities in Hacac were studied with 17 kinds of metals. In our experiments, the size of the metal sample was 1 cm^2 in the case of a sheet, and the sample was prepared so as the surface area became equal to that of the sheet in the cases of metals with other shapes. We attempted to initiate dissolution by agitating at 70°C in 10 m*l* of Hacac. The dissolution rate was determined by weighing insoluble metal fragments taken out at definite intervals. As is shown in Fig. 9, nine (aluminum, beryllium, cobalt, chromium, copper, molybdenum, nickel, titanium, and tungsten) of the 17 kinds of metals examined were scarcely dissolved at all in six hours. A similar experiment was made by Barnartt *et al.*[12]; their results were almost the same as ours. The tendencies toward the ionization of soluble metals in dissolution were found to be larger than that of hydrogen. Though the standard potentials of the elements in Hacac have never been measured, Strehlow[18] measured the potential of various metals in a non-aqueous solvent; the tendency he found agrees fairly well with that shown in Fig. 9.

Product of the Dissolution of Iron in Acetylacetone. The solution becomes red, when iron is dissolved in Hacac. The absorption spectra of both the above solution and the $Fe(acac)_3$-Hacac solution obtained in the visible region (340—600 mμ) are shown in Fig. 10. The above results show that the product of the dissolution is $Fe(acac)_3$, for the spectrum of the solution is in good agreement with that of $Fe(acac)_3$.

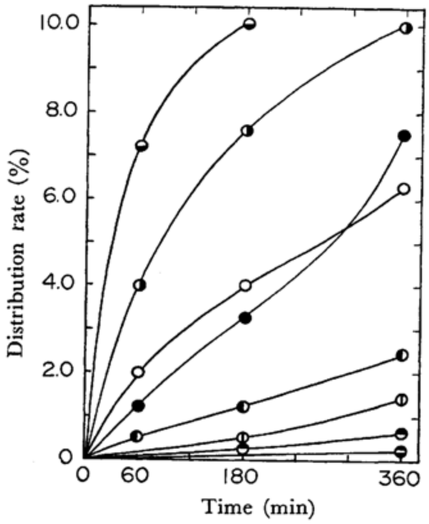

Fig. 9. Dissolution rate of various metals in Hacac.
Conditions:
Hacac, 10 m*l*
Size of metal, 10×10 mm
Temperature, 70°C
◒, Pb ◑, Mg ●, Ca ○, Zn
◐, Mn ⦶, Fe ⊖, Ce ◓, Si

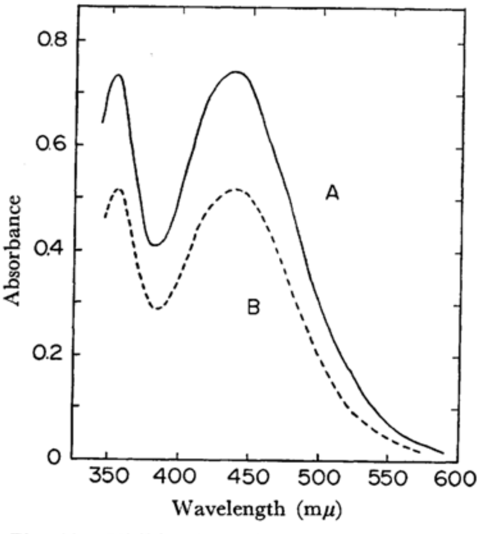

Fig. 10. Visible absorption spectra of the solution of iron in Hacac and of $Fe(acac)_3$ in Hacac.
(A) Fe: 0.0108 g/*l* Hacac
(B) $Fe(acac)_3$: 0.0487 g/*l* Hacac

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[18] H. Strehlow, *Z. Elektrochem.*, *Ber.*, *Bunsenges. Phys. Chem.*, **56**, 827 (1952).

Process of the Dissolution of Iron in Acetylacetone. The variations in the absorption spectra in the process of the dissolution of iron in Hacac are shown in Fig. 11. In the earlier steps, the absorption band at 354 mμ can not be discriminated clearly. With the passing of time, however, the absorbances at 354 and 435 mμ become larger, and at last the intensities of these two absorption bands become equal. Therefore, the spectrum may be regarded as coinciding with that of $Fe(acac)_3$.

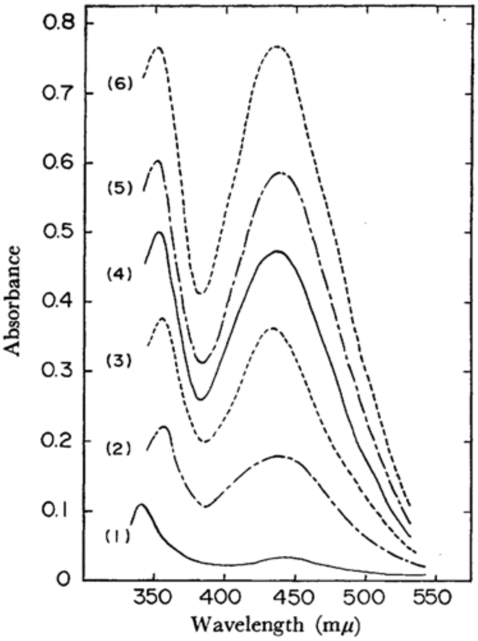

Fig. 11. Variations of the visible absorption spectrum of the solution of iron in Hacac.

On the other hand, the variations in the absorption spectra of $Fe(acac)_2$ formed from the standard iron(II) solution and Hacac are shown in Fig. 12. The behavior of the spectra shown in Fig. 12 is almost the same as that in Fig. 11. Since the $Fe(acac)_2$ with a four-coordinated-plane structure formed in the earlier step of the dissolution is stereochemically unstable, the stable form of $Fe(acac)_3$ with the octahedral six coordination is thought to be gradually formed in the solution.

In order for $Fe(acac)_2$ to be formed in a solution, it is necessary for Fe^{2+} ions to be present. Consequently, metallic iron is ionized to become Fe^{2+} ions by the action of some factor (Eq. (4)):

$$Fe \rightleftarrows Fe^{2+} + 2e^- \tag{4}$$

where the proton set free in Hacac is thought to act as follows (Eq. (5)):

$$Fe + 2H^+ \rightleftarrows Fe^{2+} + H_2 \tag{5}$$

Moreover, it was confirmed by mass spectrometry that hydrogen gas is formed during the process of the dissolution. In view of the above facts, the following reaction mechanism may be proposed for the dissolution of iron in Hacac:

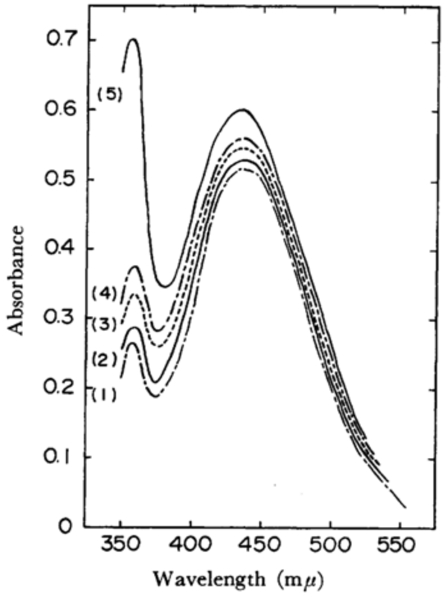

Fig. 12. Variations of the visible absorption spectrum of $Fe(acac)_2$.

$$Hacac \rightleftarrows acac^- + H^+ \tag{6}$$

$$Fe + 2H^+ \rightleftarrows Fe^{2+} + H_2$$

$$Fe^{2+} + 2acac^- \rightleftarrows Fe(acac)_2 \tag{7}$$

$$Fe(acac)_2 + acac^- \rightleftarrows Fe(acac)_3 + e^- \tag{8}$$

Dissolution of Metal in β-Diketones Except Acetylacetone. The acid strengths of β-diketones involving fluorine (HHFA, HFTA, HBTA, HTTA, *etc.*) are smaller than that of Hacac, which is 9.7.[15] Accordingly, it was thought that metal might be more readily dissolved in such fluorine-containing β-diketone solutions than in acetylacetone. Thus, its tendency in such a β-diketone solution was studied. The liquid β-diketones, such as HTFA, HHFA, and HFTA, were used in the liquid state, while the solid β-diketones, like HTTA and HBTA, were used in a solution, in which they were more enolized. The results showed that the dissolution rate of iron in a fluorine-containing β-diketone solution is ten or more times faster than that in Hacac. HHFA especially shows a powerful solubility.

On the other hand, metals were hardly dissolved at all in a solution in which a β-diketone interacted with solvents such as triethylamine and diethylamine. This fact can be explained in terms of a strong intermolecular hydrogen bond being formed between the β-diketone and the solvent.[19]

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[19] Ref. 16, p. 437; L. W. Reeves and W. G. Schneider, *Can. J. Chem.*, **36**, 793 (1958).

Accelerating Effect in the Dissolution

In the solvent extraction, the accelerating effect of the added ingredient is called "the synergistic effect."[20] A similar accelerating effect may be expected to appear in the dissolution of metals in a β-diketone solution.

Accelerating Effect of Adding an Organic Solvent in the Dissolution Phenomena. Figure 13 shows the synergistic effect observed in the case of adding another solvent to Hacac. The above experiment showed that carbon tetrachloride and glacial acetic acid were both effective as added solvents. The enol ratio of Hacac is 100% in triethylamine and 75—88% in the other solvents. The lack of solubility in triethylamine results from the strong intermolecular hydrogen bonding between solute and solvent, as has been mentioned above.[19] As a proton may be partially set free even in acetic acid, much as in Hacac, its effect is expected to persist in the solution. The above results clearly proved the dissolution of metal to be more effective in a solution containing an organic solvent than in an Hacac alone.

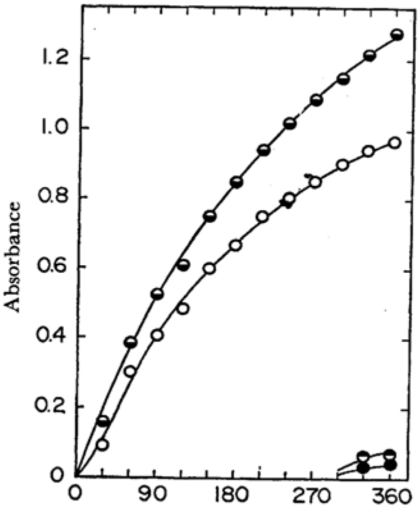

Fig. 13. Solvency of iron in Hacac solution.
◒, Hacac (5 ml) + acetic acid (5 ml) (Fe: 1.098 mg)
○, Hacac (5 ml) + CCl_4 (5 ml) (Fe: 1.020 mg)
◓, Hacac (5 ml) + benzene (5 ml) (Fe: 1.012 mg)
●, Hacac (5 ml) + cyclohexane (5 ml) (Fe: 1.011 mg)
Fe (1.155 mg) was not dissolved in Hacac (5 ml)-$N(C_2H_5)_3$ (5 ml)
Conditions:
Wavelength, 420 mμ
Reference, each solution
Cell, glass with 20 mm long

The solubility of iron in a solution containing HBTA was also examined as an example of solid β-diketones; the investigation showed that methanol was more effective than the other solvents, as is shown in Fig. 14.

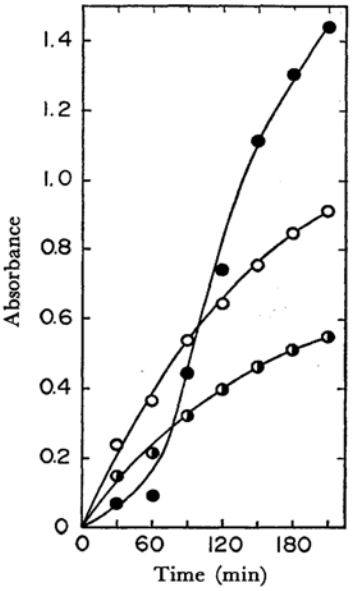

Fig. 14. Solvency of iron in HBTA solution.
●, HBTA (1 g) + Hacac (10 ml) (Fe: 1.187 mg)
○, HBTA (1 g) + methanol (10 ml) (Fe: 1.147 mg)
◑, HBTA (1 g) + CCl_4 (10 ml) (Fe: 1.184 mg)
Conditions:
Reference, each solution
Cell, glass with 20 mm long
Wavelength, 420 mμ

In order to ascertain the accelerating effect of alcohols, the tendency toward solubility of a metal in the solution was studied in detail. The results of the experiment in which eleven kinds of alcohols were employed as solvents are summarized in Table 4.

Equilibrium Reaction and Solubility of Metal in β-Diketone Involving the Fluorine-Alcohol System. We mentioned above that the effect is accelerated by adding water or alcohol in liquid β-diketone during the dissolution of metal. It must be noted that various chemical reactions can occur in a mixture. Such a point of view is important in discussing the accelerating effect in the phenomena.[9,21]

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[20] T. W. Healy, *J. Inorg. Nucl. Chem.*, **19**, 314, 328 (1961). The word "*synergism*" was first coined by Baes *et al.*; C. A. Blake, C. F. Baes, K. B. Brown, C. F. Coleman and J. C. White, Proceedings of the Second International Conference on Peaceful Uses of Atomic Energy, Geneva, 1958, 15/P/1550 (1958).

[21] K. Sato, Y. Kodama and K. Arakawa, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **87**, 821 (1966); **88**, 968 (1967).

TABLE 4. SOLVENCY OF IRON IN VARIOUS β-DIKETONE-ALCOHOL SOLUTIONS

Alcohol	β-Diketone				
	Hacac	HFTA	HTFA	HTTA	HBTA
Methyl alcohol	○	○	◎	◎	◎
Ethyl alcohol	○	○	◎	◎	◎
n-Propyl alcohol	○	○	◎	◎	◎
Isopropyl alcohol	○	○	◎	◎	◎
n-Butyl alcohol	○	○	◎	◎	◎
Isobutyl alcohol	×	×	○	○	○
n-Amyl alcohol	×	×	○	×	×
Isoamyl alcohol	×	×	×	○	○
4-Methyl-2-pentanol	×	×	○	○	○
4-Octyl alcohol	×	×	○	×	×
n-Octyl alcohol	×	×	○	○	×

◎: Well soluble ○: A little soluble ×: Hardly soluble

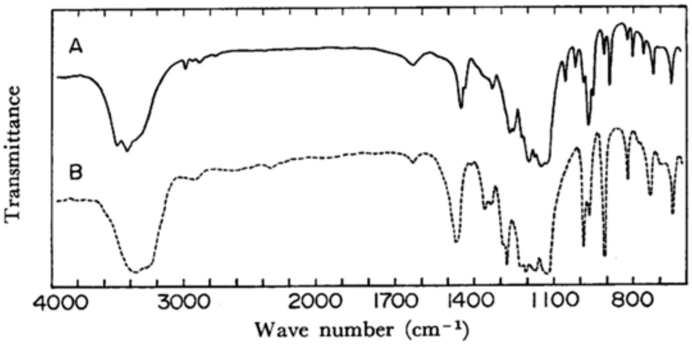

Fig. 15. Infrared spectra of the reaction product of HHFA with methanol (A) and of hexafluoroacetylacetone dihydrate (B). (KBr disk)

A white crystal was found to separate by the reaction of HHFA with water or methanol.[21] The configuration of the reaction product of HHFA with water[22] has already been studied by Schultz and Larsen,[23] who confirmed it to be hexafluoroacetylacetone dihydrate (IV), but the reaction product of HHFA with methanol has never been reported. The structure of the compound was identified on the basis of the results of elemental analysis and of the spectral investigation.

Elemental analysis showed that the compound has the formula $C_7H_{10}O_4F_6$ (Found: C, 30.77; H, 3.70%. Calcd for $C_7H_{10}O_4F_6$: C, 30.89; H, 3.57%). The IR spectrum shows absorptions at 1121 cm^{-1}(vs) due to the vibration, ν_{C-O}, of tertiary alcohol, and at 1051(w) and 1009 cm^{-1} (w) due to the ν_{C-O} of the C–O–C bond, which is illustrated in Fig. 15.

Figure 16 shows the NMR spectrum, in which signals are observed at τ 7.80, 7.66, and 4.29, with relative intensities of 1 : 3 : 1 respectively; these signals can be assigned to those due to the protons at $-C\underline{H}_2-$, $-O-C_3\underline{H}$, and $-O\underline{H}$ respectively. The UV spectrum showed no absorptions. In view of the above facts, the most reasonable identification of the compound is as 1,1,1,5,5,5-hexafluoro-(2,4-dioxy-2,4-dimethoxy)-pentane (V).*2

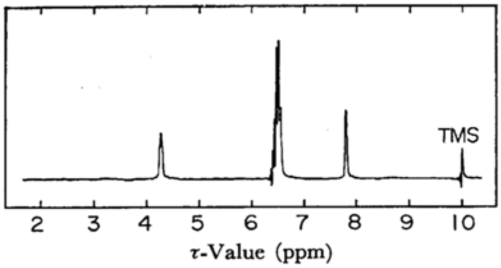

Fig. 16. Proton magnetic resonance spectrum of the reaction product of HHFA with methanol in C_2Cl_4 at 60 Mc.

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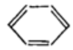
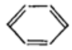
22) A. L. Henne, M. S. Newman, L. L. Quill and R. A. Staniforth, *J. Am. Chem. Soc.*, **69**, 1819 (1947).

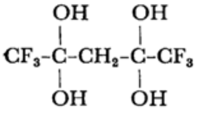
23) B. G. Schultz and E. M. Larsen, *ibid.*, **71**, 3290 (1949).

*2 Adopted later as one of the IRDC cards (No. 6777) of the Infrared Data Committee of Japan.

TABLE 5. FLUORINE RESONANCE DATA OF TRIFLUORO-SUBSTITUTED β-DIKETONE SOLUTIONS (φ; ppm)

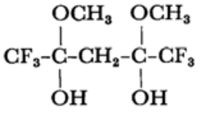
β-Diketone	Water or alcohol	$CF_3C(OH)CHCOR$	$CF_3C(OH)(OR')CH_2COR$	R	R′
HTFA	H_2O	75.4	84.6	CH_3	H
HTFA	CH_3OH	75.4	80.6	CH_3	CH_3
HTFA	C_2H_5OH	75.4	80.6	CH_3	CH_3CH_2
HTFA	C_3H_7OH	75.4	80.5	CH_3	$CH_3(CH_2)_2$
HTFA	$(CH_3)_2CHOH$	75.4	81.3	CH_3	$(CH_3)_2CH$
HTFA	C_4H_9OH	75.4	80.4	CH_3	$CH_3(CH_2)_3$
HTFA	$(CH_3)_2CHCH_2OH$	75.4	80.3	CH_3	$(CH_3)_2CHCH_2$
HTFAa)	$ClCH_2CH_2OH$	75.8	81.5	CH_3	$ClCH_2CH_2$
HTFAa)	$BrCH_2CH_2OH$	75.7	81.4	CH_3	$BrCH_2CH_2$
HTFAa)	$CNCH_2CH_2OH$	75.8	81.6	CH_3	$CNCH_2CH_2$
HTFAa)	$CH_2{=}CHCH_2OH$	76.1	81.4	CH_3	$CH_2{=}CHCH_2$
HTFAa)	$CH{\equiv}CCH_2OH$	75.6	81.4	CH_3	$CH{\equiv}CCH_2$
HFTA	H_2O	74.5	84.3		H
HFTA	CH_3OH	74.5	80.4		CH_3
HBTA	H_2O	75.1	84.5		H
HBTA	CH_3OH	75.1	80.5		CH_3
HTTA	H_2O	74.3	84.6		H
HTTA	CH_3OH	74.3	80.4		CH_3

The concentration of each solution is 50 mol%, but 50 vol% in a) mark.



$$CF_3\text{-}\underset{OH}{\overset{OH}{C}}\text{-}CH_2\text{-}\underset{OH}{\overset{OH}{C}}\text{-}CF_3$$

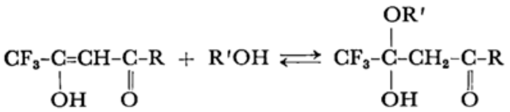
IV



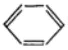
$$CF_3\text{-}\underset{OH}{\overset{OCH_3}{C}}\text{-}CH_2\text{-}\underset{OH}{\overset{OCH_3}{C}}\text{-}CF_3$$

V

The equilibrium reaction of β-diketone involving fluorine with water or alcohol was also examined.9,21) The behavior in the fluorine resonance spectra of the solution consisting of trifluoro-substituted β-diketone and water or alcohol, is summarized in Table 5. The β-diketone was clearly found to react with water or alcohol. The proton resonance spectra are shown in Figs. 17—19. A signal was observed at about δ 3 due to the methylene group, which is a singlet in water and an AB quartet in alcohol. From a consideration of the above facts, it seems most reasonable to conclude that an equilibrium reaction occurs in the solution as follows (Eq. (9)):

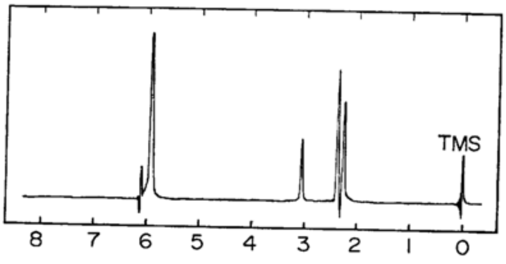


$$CF_3\text{-}\underset{OH}{C}{=}CH\text{-}\underset{\overset{\|}{O}}{C}\text{-}R + R'OH \rightleftarrows CF_3\text{-}\underset{OH}{\overset{OR'}{C}}\text{-}CH_2\text{-}\underset{\overset{\|}{O}}{C}\text{-}R \qquad (9)$$

$R = CH_3$, , , 

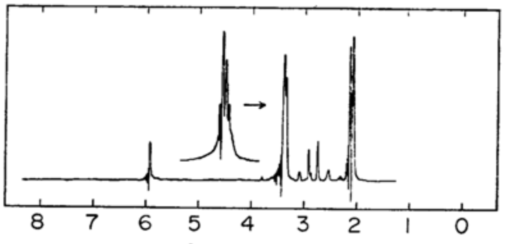
$R' = H$, CH_3, C_2H_5, C_3H_7, $(CH_3)_2CH$, C_4H_9, $(CH_3)_2CHCH_2$, $ClCH_2CH_2$, $BrCH_2CH_2$, $CNCH_2CH_2$, $CH_2{=}CHCH_2$, $CH{\equiv}CCH_2$, $PhCH_2$

The equilibrium reaction of pivaloyltrifluoroacetone with water or alcohol has already been studied.24)



δ-Value (ppm)

Fig. 17. Proton magnetic resonance spectrum of HTFA aqueous solution at 60 Mc.



δ-Value (ppm)

Fig. 18. Proton magnetic resonance spectrum of HTFA-methanol solution at 100 Mc.

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24) K. Sato, H. Ochi and K. Arakawa, This Bulletin, **42**, 1747 (1969).

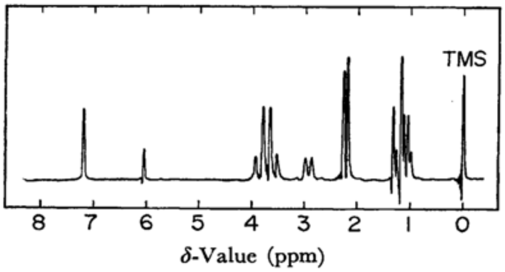


Fig. 19. Proton magnetic resonance spectrum of HTFA-ethanol solution at 60 Mc.

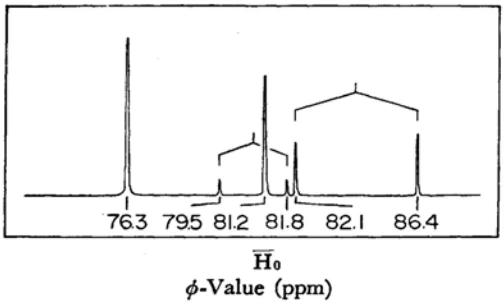
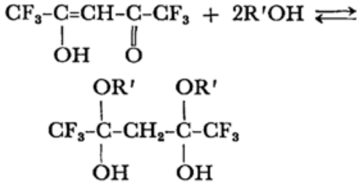


Fig. 20. Fluorine magnetic resonance spectrum of HHFA-ethylenebromohydrin solution at 56.45 Mc with $CFCl_3$ as internal standard.

Equilibrium reactions different from the above results were seen with HHFA.[21] The reaction was also confirmed by NMR spectroscopy. The fluorine resonance data of the solution of HHFA obtained with alcohol are summarized in Table 6, while the existence ratio of each state is listed in Table 7. An example of these spectra is also shown in Fig. 20. The data suggest that equilibrium states with three types, states A, B, and C, exist in the course of the reaction.

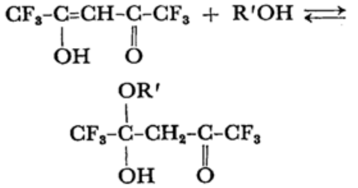
The fluorine resonance spectrum clearly proved that only a reaction on the state A is preferred in an HHFA ethanol solution. The state A may be represented by Eq. (10):



$$CF_3\text{-}\underset{OH}{\underset{|}{C}}{=}CH\text{-}\underset{O}{\underset{\|}{C}}\text{-}CF_3 + 2R'OH \rightleftarrows CF_3\text{-}\underset{OH}{\underset{|}{\overset{OR'}{\overset{|}{C}}}}\text{-}CH_2\text{-}\underset{OH}{\underset{|}{\overset{OR'}{\overset{|}{C}}}}\text{-}CF_3 \qquad (10)$$

$R' = C_2H_5$, $n\text{-}C_3H_7$, $i\text{-}C_3H_7$, $n\text{-}C_4H_9$, $CH_3(CH_2)_6CH_2$, $BrCH_2CH_2$, $CNCH_2CH_2$, $CH_2{=}CHCH_2$, $CH{\equiv}CCH_2$, $PhCH_2$

since the signal was observed at δ 2.30 with a singlet in the proton resonance spectrum. Furthermore, the AB quartets at about δ 3.30 may be due to the following reaction (Eq. (11):



$$CF_3\text{-}\underset{OH}{\underset{|}{C}}{=}CH\text{-}\underset{O}{\underset{\|}{C}}\text{-}CF_3 + R'OH \rightleftarrows CF_3\text{-}\underset{OH}{\underset{|}{\overset{OR'}{\overset{|}{C}}}}\text{-}CH_2\text{-}\underset{O}{\underset{\|}{C}}\text{-}CF_3 \qquad (11)$$

TABLE 6. FLUORINE RESONANCE DATA OF HEXAFLUOROACETYLACETONE SOLUTIONS[a] (ϕ; ppm)

Solvent	R	HFA	State A	State B		State C	
Ethyl alcohol	CH_3CH_2	—	81.6	—	—	—	—
n-Propyl alcohol	$CH_3(CH_2)_2$	76.3	81.1	—	—	—	—
Isopropyl alcohol	$(CH_3)_2CH$	75.8	80.5	78.4	81.3	79.5	81.0
Ethylenebromohydrin	$BrCH_2CH_2$	76.3	81.2	79.5	81.8	82.1	86.4
Ethylenecyanohydrin	$CNCH_2CH_2$	76.1	80.8	79.1	81.1	81.4	86.4
Allyl alcohol	$CH_2{=}CHCH_2$	76.5	81.6	—	—	—	—
Propargyl alcohol	$CH{\equiv}CCH_2$	75.8	81.9	78.8	81.6	81.1	86.2

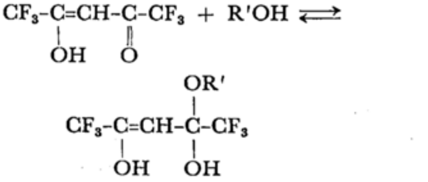
a) Each concentration is 50 vol%.

TABLE 7. EXISTENCE RATIO OF EACH STATE IN THE EQUILIBRIUM OF HEXAFLUOROACETYLACETONE SOLUTION (%)

Solvent	HHFA		State A		State B		State C	
	23°C	45°C	23°C	45°C	23°C	45°C	23°C	45°C
Ethyl alcohol	—	†	100	†	—	†	—	†
n-Propyl alcohol	12	18	88	82	—	†	—	†
Isopropyl alcohol	34	45	18	15	37	30	11	10
Ethylenebromohydrin	32	†	33	†	27	†	8	†
Ethylenecyanohydrin	34	†	54	†	6	†	6	†
Allyl alcohol	20	†	80	†	—	†	—	†
Propargyl alcohol	40	41	48	41	6	†	6	9

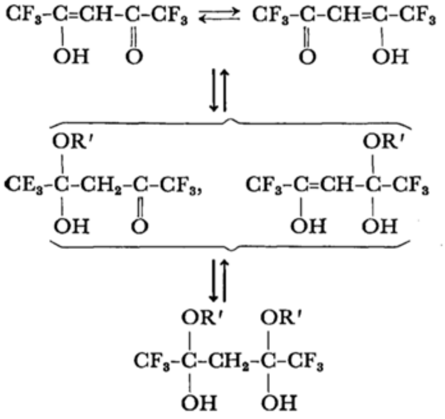
† These values were not measured.

while the multiplet at about δ 4.70 is due to the methine group formed by the following reaction (Eq. (12)):



$$\mathrm{CF_3\text{-}\underset{OH}{C}{=}CH\text{-}\underset{O}{\overset{}{C}}\text{-}CF_3 + R'OH \rightleftharpoons CF_3\text{-}\underset{OH}{C}{=}CH\text{-}\overset{OR'}{\underset{OH}{C}}\text{-}CF_3} \qquad (12)$$

In the proton resonance spectrum of the isopropanol solution, the signal intensity at δ 3.30 with the AB quartet is greater than that at about δ 4.70. The reactions involving the states B and C were found to be due to the reactions (12) and (11) respectively. From these results, the correlation in the equilibrium of HHFA with various alcohols may be summarized as follows:



$$\mathrm{CF_3\text{-}\underset{OH}{C}{=}CH\text{-}\underset{O}{C}\text{-}CF_3 \rightleftharpoons CF_3\text{-}\underset{O}{C}\text{-}CH{=}\underset{OH}{C}\text{-}CF_3}$$

$$\Big\downarrow\!\!\uparrow$$

$$\overbrace{\mathrm{CE_3\text{-}\overset{OR'}{\underset{OH}{C}}\text{-}CH_2\text{-}\underset{O}{C}\text{-}CF_3,\quad CF_3\text{-}\underset{OH}{C}{=}CH\text{-}\overset{OR'}{\underset{OH}{C}}\text{-}CF_3}}$$

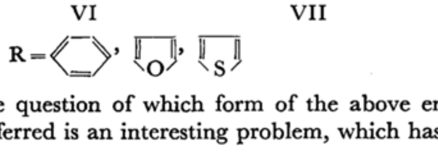
$$\Big\downarrow\!\!\uparrow$$

$$\mathrm{CF_3\text{-}\overset{OR'}{\underset{OH}{C}}\text{-}CH_2\text{-}\overset{OR'}{\underset{OH}{C}}\text{-}CF_3}$$

$R' = C_2H_5$, C_3H_7, $(CH_3)_2CH$, $BrCH_2CH_2$,
$CNCH_2CH_2$, $CH_2{=}CHCH_2$, $CH{\equiv}CCH_2$,
C_4H_9, C_8H_{17}, $PhCH_2$

Fluorine-containing β-diketones are generally reactive. The reactivity may be explained by considering that the carbon atom adjacent to the trifluoromethyl group is activated by the *I* effect of the functional group with the fluorine atom, which has a strong electro-negativity. The dissolution of metal in such solutions is remarkably accelerated, as has been mentioned above. The reason for this is, however, not clear; the cause may be in the acid strength of β-diketone alone or in the presence of such an equilibrium.

Preferred Enol Form of Trifluorosubstituted β-Diketone and Solubility of Metal. β-Diketones with a trifluoromethyl group are thought to take the following enol forms (Eq. (13)):[5–9]



$$\mathrm{\underset{VI}{CF_3\text{-}\underset{OH}{C}{=}CH\text{-}\underset{O}{C}\text{-}R} \rightleftharpoons \underset{VII}{CF_3\text{-}\underset{O}{C}\text{-}CH{=}\underset{OH}{C}\text{-}R}} \qquad (13)$$

The question of which form of the above enols is preferred is an interesting problem, which has been discussed in only a few reports.[5,8,25] On the basis of the assumption that a conjugate system must be formed between the R ring and the carbonyl group in the β-diketone molecule and the UV spectrum may become remarkable due to the polarity of the solvent;[26] the investigation discussed below was undertaken in order to determine the preferred enol form.[10]

The UV spectra of HBTA and HTTA in various solvents are illustrated in Figs. 21 and 22 respectively. In view of the absorption band at about 260 mμ, the behavior of HBTA is clearly different from that of HTTA: the intensity of absorption varies in HBTA, but not in HTTA. The variations according to polar and non-polar solvents suggest that a conjugate system with a carbonyl group is formed adjacent to the aromatic ring. Accordingly, the preferred enol forms of HBTA and HTTA may be regarded as being VI and VII respectively. The results of the above studies support the theory which Pukanic *et al.*[26] derived from their study on the interaction between

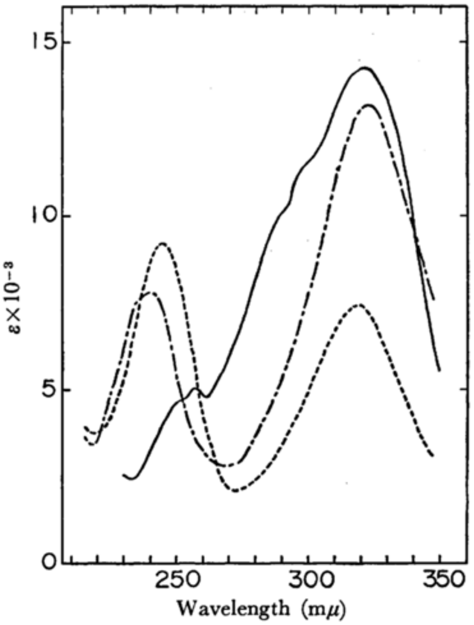


Fig. 21. UV spectrum of HBTA.
Solvent: ——, *n*-heptane
—·—, ethanol
----, water

---

[25] Pukanic *et al.* have shown from the fluorine magnetic resonance frequency of enolic HTTA and HHFA in CCl_4, in the absence and in the presence of various concentrations of TBP, that the preferred enol form of HTTA is VII; G. Pukanic, N. C. Li, W. S. Brey, Jr., and G. B. Savitsky, *J. Phys. Chem.*, **70**, 2899 (1966).

[26] For one of the examples, see M. Hirota, "The Interpretations of UV and Visible Spectra," Kyoritsu Shuppan, Tokyo (1967), p. 81.

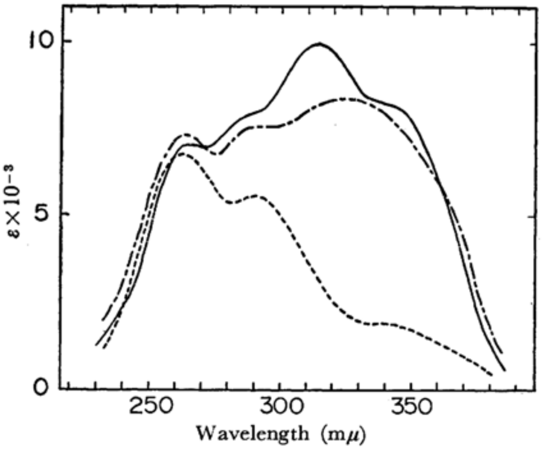
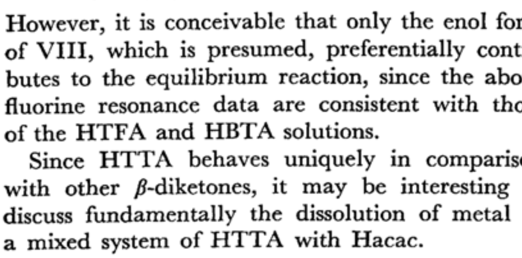


Fig. 22. UV spectrum of HTTA.
Solvents: ——, *n*-heptane
—·—, ethanol
----, water

HTTA and tributylphosphate (TBP) by means of the fluorine resonance spectra.

As Figs. 21 and 22 show, no special abnormalities are recognized in the so-called "*enol absorption band*" in the region with wavelengths longer than 300 mμ, so it may be concluded that the above equilibrium reaction exerts an essential influence on the molar extinction coefficient (ε). This influence must, therefore, be explained as the mutual effect of the keto-enol tautomerism with the equilibrium reaction in the solution. As the enol form of VII is preferred in the HTTA solution, the following equilibrium is also possible between HTTA and alcohol (Eq. (14)):



$$\underset{\text{VIII}}{CF_3\text{-}\underset{\displaystyle O}{\underset{\|}{C}}\text{-}CH{=}\underset{\displaystyle OH}{\underset{|}{C}}\text{-}C_4H_3S} + R'OH \rightleftharpoons CF_3\text{-}\overset{\displaystyle OR'}{\overset{|}{\underset{\displaystyle OH}{\underset{|}{C}}}}\text{-}CH{=}\underset{\displaystyle OH}{\underset{|}{C}}\text{-}C_4H_3S \qquad (14)$$

R′=H, CH_3, $(CH_3)_2CH$, $CNCH_2CH_2$, $PhCH_2$, *etc.*

However, it is conceivable that only the enol form of VIII, which is presumed, preferentially contributes to the equilibrium reaction, since the above fluorine resonance data are consistent with those of the HTFA and HBTA solutions.

Since HTTA behaves uniquely in comparison with other β-diketones, it may be interesting to discuss fundamentally the dissolution of metal in a mixed system of HTTA with Hacac.

Conclusion

Concerning the dissolution of metal in a β-diketone solution, the effective factors, the process of the dissolution, and the accelerating effect in dissolution were studied in detail. The effective factors were shown to be oxygen, co-existing water, and the dissociated proton in the solution.

The phenomena of the dissolution were expected to be applied effectively not only to the analysis of iron and steel, but also of other metals and alloys. For example, it is possible to establish new analytical methods by using these phenomena together with gas chromatography, polarography, the atomic absorption method, and so on. Part of an attempt to do so has already been reported.[27–32]

The problems related to the preferred enol forms of trifluorosubstituted β-diketones and the equilibrium reactions of fluorine-containing β-diketones with water or alcohols are interesting even in the field of organic chemistry; moreover, the solubilities of metals in these solutions must also involve a large number of significant problems.

The unique behavior of HTTA is seen not only in the dissolution of metal, but also in the solvent extraction. A thorough investigation, from a similar point of view, may be expected to establsih the cause of the series of phenomena, so the problem may be left as an interesting one for the future.

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