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The Oxidation of Acetylacetone in the Presence of Cobaltous Ions

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Concerning the oxidation of toluene and *p*-xylene with atmospheric oxygen at 90°C in glacial acetic acid in the presence of cobaltous acetate and acetylacetone (HAAH), it was found that the reaction proceeds smoothly only at the mole ratio of $[\mathrm{HAAH}]/[\mathrm{Co}^{2+}]=2$. When the absorption rate of oxygen was then measured for acetic acid solutions containing cobaltous ions and HAAH, the following results were obtained:

at $[\mathrm{HAAH}]/[\mathrm{Co}^{2+}]\leqq 3$, $-\mathrm{d}[\mathrm{O_2}]/\mathrm{d}t=K_\mathrm{a}[\mathrm{HAAH}]^{1/2}[\mathrm{Co}^{2+}]^{-1/3}$

at $[\mathrm{HAAH}]/[\mathrm{Co}^{2+}]\geqq 4$, $-\mathrm{d}[\mathrm{O_2}]/\mathrm{d}t=K_\mathrm{b}[\mathrm{HAAH}][\mathrm{Co}^{2+}]^{1/4}$

These rates agree well with those derived by means of elementary equations in the radical chain reactions. It was further supposed, on the basis of the elementary equations, that active intermediates, such as Co^{3+}, $[\mathrm{Co}^{3+}(\mathrm{AAH}^-)_2]^+$, and some radicals, were produced smoothly at the mole ratio of $[\mathrm{HAAH}]/[\mathrm{Co}^{2+}]=2$. However, ketones, such as acetonylacetone and ethyl acetoacetate, were still active even at the mole ratio of $[\mathrm{ketone}]/[\mathrm{Co}^{2+}]=3$. This seems to stem from the differences in complex stabilities between cobalt and HAAH or other ketones.

It was reported by Brill[1] in 1960 that alkylbenzenes are effectively oxidized when an alkylbenzene in glacial acetic acid in the presence of cobaltous acetate tetrahydrate and ethyl methyl ketone (a ketone containing an α-methylene group) is allowed to contact with oxygen while being sufficiently stirred at 90°C under an atmospheric pressure. This report attracted the present authors, since it enabled us to anticipate some effects based on the chelate formation between cobalt and such a ketone as acetylacetone, and provided a clue as to the nature of the oxidation mechanism.

p-Xylene was then oxidized under the same conditions as were used in Brill's method, except for the utilization of acetylacetone in its various mole ratios to cobalt; it was thus found that terephthalic acid could be obtained only at the cobalt: acetylacetone mole ratio of 1 : 2. Since this fact was very interesting to the present authors, a study was primarily made of the oxidation of acetylacetone in the presence of cobaltous ions by measuring the absorption rate of oxygen.

With a view to identifying the final products in the oxidation of acetylacetone, acetylacetone was oxidized in propionic acid much as in glacial acetic acid, and the oxidation products were examined by gas chromatography.

Experimental

Reagents.—The *p*-xylene obtained from the Maruzen Sekiyu Co., Ltd., was treated with sulfuric acid, sodium hydroxide and water, and recrystallized twice; the distillate with a b. p. of 138.5°C was used. Toluene was treated much as was *p*-xylene, but the distillate with a b. p. of 110.5°C was used. The cobaltous acetate tetrahydrate and the glacial acetic acid were both of an analytical reagent grade. Acetylacetone was distilled, and the distillate with a b. p. of 137°C was used. Cobaltous propionate was synthesized from propionic acid and cobaltous carbonate, and recrystallized from ethanol and diethyl ether. The cobalt was determined chelatometrically by using ethylenediaminetetraacetic acid and murexide. The distillate with a b. p. of 141°C was used for propionic acid.

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[1] W. F. Brill, *Ind. Eng. Chem.*, **52**, 837 (1960).

TABLE I. RELATIONSHIP BETWEEN THE MOLE RATIOS OF CHARGED KETONES TO COBALT AND THE OXIDATION PRODUCTS

No.	Ketones containning α-methylene group	mol./l.	*p*-Xylene mol./l.	$Co(OAc)_2 \cdot 4H_2O$ mol./l.	Terephthalic acid
1	Ethyl methyl ketone* ($CH_3CH_2COCH_3$)	0.2	1	0.1	(yield** about 65%)
2	Acetylacetone ($CH_3COCH_2COCH_3$)	0.1	1	0.1	impossible
		0.2	1	0.1	(yield about 75%)
		0.3	1	0.1	impossible
		0.4	1	0.1	impossible
		0.5	1	0.1	impossible
3	Acetonylacetone ($CH_3COCH_2CH_2COCH_3$)	0.2	1	0.1	yield 40% (toluic acid about 40%)
		0.3	1	0.1	yield 40% (toluic acid about 40%)
4	Ethyl acetoacetate ($CH_3COCH_2COOC_2H_5$)	0.2	1	0.1	yield 40% (toluic acid about 20%)
		0.3	1	0.1	yield 40% (toluic acid about 20%)
			Toluene mol./l.		Benzoic acid
5	Acetylacetone	0.2	1	0.1	possible
		0.3	1	0.1	impossible

* The same conditions as in Brill's experiment.

** The yields are given by the mole per cent of the oxidation products to charged *p*-xylene.

The Oxidation of *p*-Xylene and Toluene.—To 200 ml. of glacial acetic acid, 0.02 mol. of cobaltous acetate tetrahydrate, 0.2 mol. of *p*-xylene or toluene, and 0.02—0.1 mol. of a ketone such as acetylacetone, acetonylacetone, ethyl acetoacetate and ethyl methyl ketone are added. The solution is then placed in contact with oxygen for 24 hr. at 90°C, 1 atm., and 800—1000 r. p. m.

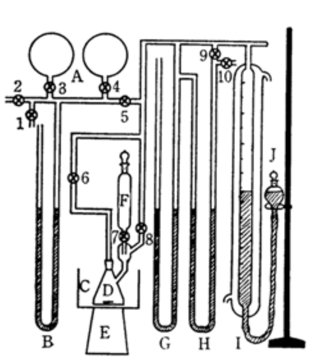


Fig. 1. An apparatus for the measurement of oxygen absorption rate.
A: gas storage B: manometer (charged with mercury) C: thermostat D: reaction vessel E: magnetic stirrer F: funnel for supplying sample G: manometer (charged with mercury) H: manometer (charged with dibuthylphthalate) I: gas burette J: mercury pool

The Absoption Rate of Oxygen.—The absorption rate of oxygen was measured by the apparatus shown in Fig. 1. The apparatus was operated as follows: all the cocks except the cocks 2, 7 and 10 are opened after J has been lowered, and the system is made completely vacuous through the cock 1. The cocks 1 and 5 are then closed, and A is filled with more than 1 atm. of oxygen through the cock 2. Then the cock 2 is closed, and the oxygen gas pressure is adjusted to the atmospheric pressure by opening the cock 5 and reading the manometer, G, charged with mercury. The cock 9 is closed, and the cock 10 is opened. To the reaction vessel, D, 50 ml. of glacial acetic acid and cobaltous acetate are added, and the solution is heated at 60±0.2°C, The liquid surfaces of the manometer, H, charged with dibutyl phthalate are adjusted to the same level by moving J vertically. Acetylacetone is added through the cock 7, and the reaction is started.

During the reaction, the liquid surfaces of the manometer, H, are held on the same level by moving J; thereby the oxygen gas pressure is always maintained at 1 atm. The absorption rate of oxygen is measured by reading the gas burette, I, at definite intervals. Oxygen is supplied to the system by closing the cocks 6 and 8, lowering J, and introducing oxygen through the cock 5 until the liquid surfaces of H reach just the same level. I is read at once, and measurement is continued after the opening of the cocks 6 and 8.

The Identification of the Oxidation Products of Acetylacetone.—Since the absorption rate of oxygen in propionic acid was confirmed to be quite similar to

TABLE II. OXYGEN ABSORPTION IN VARIOUS MOLE RATIOS OF ACETYLACETONE TO COBALT

No.	Co^{2+}		HAAH		Mole ratios Co^{2+} : HAAH	O_2 absorbed		Induction period min.
	mol./l.	mol.*	mol./l.	mol.*		ml.**	mol.	
1	0.1	0.005	0.05	0.0025	1 : 0.5	93.5	0.0038	1
2	0.1	0.005	0.10	0.005	1 : 1	177.2	0.0072	2
3	0.1	0.005	0.20	0.010	1 : 2	275.4	0.0113	6
4	0.1	0.005	0.30	0.015	1 : 3	319.7	0.0131	15
5	0.1	0.005	0.40	0.020	1 : 4	370.7	0.0155	26
6	0.1	0.005	0.50	0.025	1 : 5	444.2	0.0187	47
7	0.1	0.005	0.60	0.030	1 : 6	499.1	0.0210	79
8	0.1	0.005	0.70	0.035	1 : 7	545.3	0.0229	148
9	0.01	0.0005	0.20	0.010	1 : 20	274.0	0.0111	90
10	0.02	0.001	0.20	0.010	1 : 10	286.6	0.0117	35
11	0.04	0.002	0.20	0.010	1 : 5	296.2	0.0125	18
12	0.05	0.0025	0.20	0.010	1 : 4	273.9	0.0115	11
13	0.07	0.0035	0.20	0.010	1 : 3	282.0	0.0118	7
14	0.10	0.005	0.20	0.010	1 : 2	275.4	0.0113	6
15	0.20	0.010	0.20	0.010	1 : 1	263.2	0.0111	2

* Mol. in 50 ml. HOAc. ** ml. at 25°C

that in glacial acetic acid, except for a slight elongation of the induction period, the oxidation products of acetylacetone were identified as follows: Acetylacetone in 1.5×10^{-2} mol. and cobaltous propionate in 5×10^{-3} mol. are dissolved in 50 ml. propionic acid, and the solution is placed in contact with oxygen for 3 hr. at 60°C, 1 atm. Then the solution is distilled by introducing the vapor of methanol or ethanol, and the acids in the distillate are directly converted into their esters. After esterification, the esters are distilled, and the residues are diluted with water and then extracted with ether. Both the extract and the distillate are examined by gas chromatography.

Results

The Oxidation of *p*-Xylene and Toluene.—

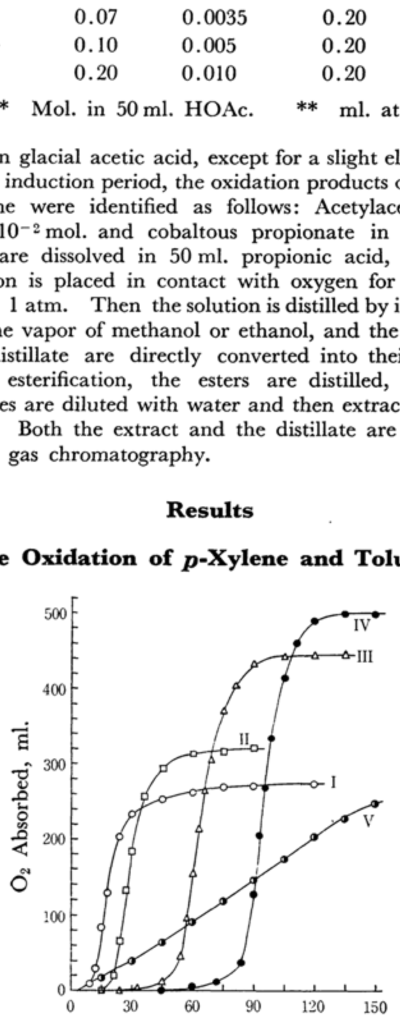


Fig. 2. Relationships between the amount of oxygen absorbed and the reaction time.
Reaction temp.: 60±0.2°C, $[Co^{+2}]$: 0.1 mol./l.
I: 0.2 mol. HAAH/l. II: 0.3 mol. HAAH/l.
III: 0.5 mol. HAAH/l. IV: 0.6 mol. HAAH/l.
V: 0.2 mol. HAAH/l. + 0.5 mol. *p*-xylene/l.

For the oxidation of *p*-xylene in the presence of 0.02 mol. of cobaltous acetate and 0.04 mol. of acetylacetone, the solution gradually changed its color from violet to brown, and finally to dark green after about 6 hours' reaction, whereupon a small amount of terephthalic acid began to deposit.

In any mole ratios other than acetylacetone: cobalt=2 : 1, terephthalic acid was not identified in 24 hours' reaction, and the unreacted *p*-xylene was found in the oily phase after the reaction mixture had been diluted with water.

When the mole ratios of acetonylacetone or ethyl acetoacetate to cobaltous acetate were 2 : 1 and 3 : 1 respectively, however, terephthalic acid was identified after 7 hours' reaction.

For the oxidation of toluene, benzoic acid was obtained in a good yield at only the mole ratio of acetylacetone : cobalt=2 : 1.

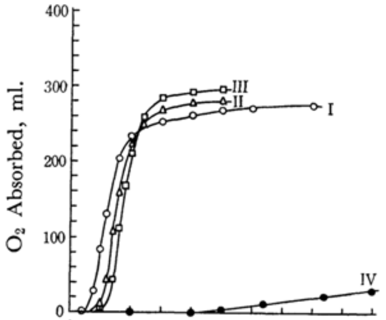
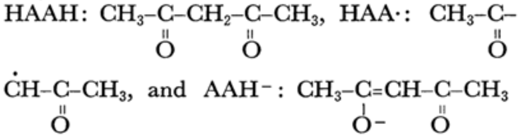


Fig. 3. Relationships between the amount of oxygen absorbed and the reaction time.
Reaction temp.: 60±0.2°C, [HAAH]: 0.2 mol./l.
I: 0.1 mol. Co^{2+}/l. II: 0.05 mol. Co^{2+}/l.
III: 0.04 mol. Co^{2+}/l.
IV: 0.1 mol. $Co^{3+}(AAH^{-})_3$

The Oxidation of Acetylacetone.—The absorption rate of oxygen was measured for the oxidation of acetylacetone in the absence of alkylbenzene; the results obtained are shown in Table II. As can be seen from Experiments Nos. 1—8 in Table II, the amount of oxygen gas absorbed increases with the concentration of HAAH at 0.1 mol./l. cobaltous acetate; the relationship between the amount of oxygen gas absorbed and the concentration of HAAH is shown in Fig. 4. Here, HAAH, HAA· and AAH$^-$ are given by the following:



HAAH: $CH_3-\underset{\underset{O}{\|}}{C}-CH_2-\underset{\underset{O}{\|}}{C}-CH_3$, HAA·: $CH_3-\underset{\underset{O}{\|}}{C}-\dot{C}H-\underset{\underset{O}{\|}}{C}-CH_3$, and AAH$^-$: $CH_3-\underset{\underset{O^-}{|}}{C}=CH-\underset{\underset{O}{\|}}{C}-CH_3$

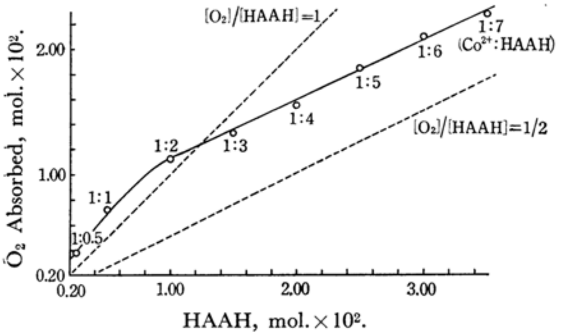


Fig. 4. Relationships between the mole ratio of [HAAH]/[Co^{2+}] and the amount of O_2 absorbed; [Co^{2+}]: 0.1 mol./l.

Figure 4 shows that the mole ratios of the [HAAH] to the [O_2] absorbed are equal to 1 and 2 at [HAAH]/[Co^{2+}]<2 and [HAAH]/[Co^{2+}]>3 respectively.

In Experiments Nos. 9—15, the concentration of cobaltous ions was varied against 0.2 mol./l. HAAH, but the amounts of oxygen gas absorbed were almost constant. These results are shown in Fig. 5. The straight line in Fig. 5 is represented by $t=k([HAAH]^2/[Co^{2+}])K^{1/4}$, where t is referred to the induction period and K, to the [HAAH]/[Co^{2+}]. It may be seen from the above equation that t does not only depend on the mole ratio of HAAH to Co^{2+}, but also on their concentrations.

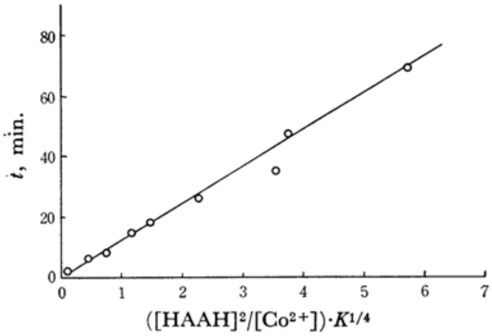


Fig. 5. Relationships between the introduction period, t, and ($[HAAH]^2/[Co^{2+}]$)·$K^{1/4}$.

After the induction period, the temperature of the reaction mixture increased in accordance with the changes in color from pink to dark green. This color change is considered to be due to the formation of cobaltic ions. After the absorption of oxygen had finished, the solution was red at the mole ratio of [HAAH]/[Co^{2+}]<3, but dark green at [HAAH]/[Co^{2+}]>4. When the dark-green substance was extracted into the benzene layer, the aqueous layer remained wine-red. The spectrophotometric absorption curves of the benzene and aqueous layers showed their maximum absorptions at 600 and 510 mμ respectively; they were compared with those of $Co^{2+}(OAc^-)_2$, $Co^{2+}(AAH^-)_2$, and $Co^{3+}(AAH^-)_3$.

The Oxidation Rate of Acetylacetone.—The relationship between the absorption rate of oxygen and the concentrations of HAAH or Co^{2+} are shown in Tables III and IV. Since there are linear relations between log(d[O_2]/dt) and log[HAAH], and log(d[O_2]/dt) and log[Co^{2+}] respectively, the absorption rates of oxygen are given

TABLE III. THE CONCENTRATION OF ACETYLACETONE AND THE OXYGEN ABSORPTION RATE

Reaction temp.: 60±0.2°C

Oxygen pressure: 1 atm., [Co^{2+}]: 0.1 mol./l.

No.	d[O_2]dt* ml. sec^{-1}	log-(d[O_2]/dt)	[HAAH] mol. l^{-1}	log-[HAAH]	Apparent rate constant
1	8.56	0.9325	0.05	−1.3009	17.8
2	11.64	1.0660	0.1	−1.0000	17.1
3	16.13	1.2076	0.2	−0.6990	16.8
4	19.56	1.2914	0.3	−0.5229	16.6
5	15.33	1.1852	0.4	−0.3979	68.0
6	19.73	1.2952	0.5	−0.3010	70.0
7	23.52	1.3715	0.6	−0.2218	69.5
8	24.36	1.3867	0.7	−0.1549	61.6

TABLE IV. THE CONCENTRATION OF COBALT AND THE OXYGEN ABSORPTION RATE

Reaction temp.: 60±0.2°C

Oxygen pressure: 1 atm., [HAAH]: 0.1 mol./l.

No.	d[O_2]/dt* ml. sec^{-1}	log-(d[O_2]/dt)	[Co^{2+}] mol. l^{-1}	log-[Co^{2+}]	Apparent rate constant
9	13.45	1.1287	0.01	−2.0000	212
10	15.67	1.1951	0.02	−1.6990	208
11	18.31	1.2627	0.04	−1.3979	205
12	20.92	1.3220	0.05	−1.3010	221
13	19.71	1.2947	0.07	−1.1549	18.1
14	16.13	1.2076	0.10	−1.0000	16.8
15	14.25	1.1538	0.20	−0.6990	18.6

* These values were obtained by differentiating the oxygen absorption curves at 25°C.

as follows:

at $[\mathrm{HAAH}]/[\mathrm{Co}^{2+}] \leq 3$,

$$-\mathrm{d}[\mathrm{O}_2]/\mathrm{d}t = k_{\mathrm{a}}[\mathrm{HAAH}]^{1/2}[\mathrm{Co}^{2+}]^{-1/3}$$

at $[\mathrm{HAAH}]/[\mathrm{Co}^{2+}] \geq 4$,

$$-\mathrm{d}[\mathrm{O}_2]/\mathrm{d}t = k_{\mathrm{b}}[\mathrm{HAAH}][\mathrm{Co}^{2+}]^{1/4}$$

Since the concentration of HAAH is enough in Experiments Nos. 5—8, the dissolution velocity of oxygen into the solution is considered to be rate-determining; therefore, their apparent rate constants are supposed to be smaller than those in Nos. 9—12. That the apparent rate constants in Nos. 5—8 are much smaller than those in Nos. 9—12 is due to the facts that the dissolution velocity of oxygen into the solution is rate-determining and that it is smaller than the consumption velocity of oxygen in the oxidation reaction. It may, therefore, be supposed that the apparent rate constants in the case of $[\mathrm{HAAH}]/[\mathrm{Co}^{2+}] \geq 4$ are equal to those in Nos. 9—12.

The Identification of the Oxidation Products of HAAH.—The sample distilled with the vapor of methanol was analyzed by gas chromatography under the following conditions: carrier gas: hydrogen; flow rate: 30 ml./min.; column: dioctyl phthalate, and column temperature: 50°C. It was confirmed from the gas chromatogram that there were aldehydes, methyl formate, methanol (solvent), methyl acetate or acetone, and methyl propionate. The distillate with the vapor of ethanol and the extracts with ether from the residues after esterification were also analyzed, under the same conditions as above except for the column temperature, which was here 60°C or 100°C respectively. The following substances were confirmed: ethyl formate, ethanol (solvent), ethyl acetate, and ethyl propionate for the former, in which acetone was negative; and ether (solvent), ethyl propionate, and ethyl pyruvate for the latter. On the basis of the gas chromatographic data and the detection of aldehyde with an ammoniacal silver nitrate solution, it was concluded that the oxidation products of HAAH were composed of acetic acid and formic acid as the major constituents, and of formaldehyde, acetaldehyde and pyruvic acid as the minor constituents.

Discussion

The oxidation mechanism of HAAH in glacial acetic acid in the presence of cobaltous ions is considered to be as follows:

In the Case of $[\mathrm{HAAH}]/[\mathrm{Co}^{2+}] \leq 3$:

It is assumed that the reaction proceeds in accordance with the following radical chain reaction, in which the rate constants are given by the k_1—k_{10} value:

Initiation

$$\left\{\begin{array}{lr} \mathrm{Co}^{2+} + \mathrm{AAH}^- \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathrm{Co}^{2+}(\mathrm{AAH}^-) & V_1,\ V_{-1}\ (1) \\ \mathrm{Co}^{2+}(\mathrm{AAH}^-) + \mathrm{O}_2 \overset{k_2}{\rightarrow} & \\ \qquad \mathrm{Co}^{2+} + \mathrm{HAA}\cdot + \cdot\mathrm{O}_2{}^- & V_2\ (2) \end{array}\right.$$

Propagation

$$\left\{\begin{array}{lr} \mathrm{HAA}\cdot + \mathrm{O}_2 \overset{k_3}{\rightarrow} \mathrm{HAAO}_2\cdot & V_3\ (3) \\ \mathrm{HAAO}_2\cdot + \mathrm{HAAH} \overset{k_4}{\rightarrow} & \\ \qquad \mathrm{HAAO}_2\mathrm{H} + \mathrm{HAA}\cdot & V_4\ (4) \\ \left(\begin{array}{l} \mathrm{HAAO}_2\cdot + \{\mathrm{Co}^{2+}(\mathrm{AAH}^-)_2\}\cdots\mathrm{O}_2 \\ \qquad \overset{k_5}{\rightarrow} \text{complex} \\ \text{Complex} \overset{k_6}{\rightarrow} \\ \qquad 2\mathrm{Co}^{2+}(\mathrm{AAH}^-)_2\mathrm{O}_2 + \mathrm{HAA}\cdot \end{array}\right. & \begin{array}{r} \\ V_5\ (5) \\ \\ V_6\ (6) \end{array} \end{array}\right.$$

Branched propagation

$$\left\{\begin{array}{lr} \mathrm{Co}^{2+} + \mathrm{HAAO}_2\mathrm{H} \overset{k_7}{\rightarrow} & \\ \qquad \mathrm{Co}^{3+} + \mathrm{HAAO}\cdot + \mathrm{OH}^- & V_7\ (7) \\ \mathrm{Co}^{3+} + \mathrm{HAAH} \overset{k_8}{\rightarrow} \mathrm{Co}^{2+} + \mathrm{HAA}\cdot + \mathrm{H}^+ & V_8\ (8) \\ \mathrm{HAAO}\cdot + \mathrm{HAAH} \overset{k_9}{\rightarrow} \mathrm{HAAOH} + \mathrm{HAA}\cdot & V_9\ (9) \end{array}\right.$$

Termination

$$\{2\mathrm{HAAO}_2\cdot \overset{k_{10}}{\rightarrow} \text{Inactive products} \qquad V_{10}\ (10)$$

In the initiation reaction, the 1 : 1 cobaltous chelate is made to react with oxygen to produce HAA·, while the HAA· induced the propagation reactions, which consist of two courses: 3—4, and 3—5—6. The hydroperoxide produced in the reaction 4 induces the reaction 7—9. It seems to be reasonable to suppose the branched reaction, since the solution during the oxidation shows the dark green usually associated with the cobaltic state. It is considered that in the reaction 5 the bridged compound, $\{(\mathrm{AAH}^-)_2\mathrm{Co}^{2+}\cdots\mathrm{O}_2\cdots\mathrm{Co}^{2+}(\mathrm{AAH}^-)_2\}$,(2) in which each cobalt has a vacant position on the coordination sphere, is coordinated of with $\mathrm{HAAO}_2\cdot$ to produce a complex compound.(3)

The absorption rate of oxygen is given by Eq. a·1:

$$-\mathrm{d}[\mathrm{O}_2]/\mathrm{d}t = V_3 = k_3[\mathrm{HAA}\cdot][\mathrm{O}_2] \qquad (\mathrm{a}\cdot 1)$$

Under a steady state, the following i—iii are assumed:

i) By assuming $\mathrm{d}[\mathrm{HAAO}_2\cdot]/\mathrm{d}t = 0$, $V_3 = V_4 + V_5 + V_{10}$:

Here, V_{10} is neglected, since the chain is long enough and since $V_{\mathrm{prop.}} \gg V_{\mathrm{term.}}$.

By assuming that the ratio, C, of V_5 to V_4 is constant and that the reaction 5 is the rate-determining step in the course 5—6, Eq. a·1 is rewritten by Eq. a·2:

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(2) A. Werner and A. Mylius, *Z. Anog. Chem.*, **16**, 1245 (1898).

(3) For example, P. George and A. Robertson, *Trans. Faraday Soc.*, **42**, 217 (1946).

$$-\mathrm{d}[\mathrm{O_2}]/\mathrm{d}t = (1+C)V_4$$
$$= (1+C)k_4[\mathrm{HAAO_2\cdot}][\mathrm{HAAH}] \qquad (\mathrm{a}\cdot 2)$$

ii) By assuming $V_{\mathrm{init.}} = V_{\mathrm{term.}}$, Eq. b·1 is obtained:

$$k_2[\mathrm{Co^{2+}(AAH^-)}][\mathrm{O_2}] = k_{10}[\mathrm{HAAO_2\cdot}]^2 \qquad (\mathrm{b}\cdot 1)$$

By supposing $k_1/k_{-1} = K_{\mathrm{m}}$ in the reaction 1:

$$[\mathrm{Co^{2+}(AAH^-)}] = K_{\mathrm{m}}[\mathrm{Co^{2+}}][\mathrm{AAH^-}]$$

By introducing $\mathrm{HAAH} \overset{Ka}{\rightleftarrows} \mathrm{AAH^-} + \mathrm{H^+}$, in which K_{a} is referred to the dissociation constant, $K_{\mathrm{a}} = [\mathrm{AAH^-}][\mathrm{H^+}]/[\mathrm{HAAH}]$; therefore, $[\mathrm{AAH^-}] = K_{\mathrm{a}}^{1/2}[\mathrm{HAAH}]^{1/2}$.

Hence, Eq. b·1 is expressed by b·2:

$$[\mathrm{HAAO_2\cdot}]^2 = (k_2\cdot K_{\mathrm{m}}\cdot K_{\mathrm{a}}^{1/2}/k_{10})\cdot$$
$$[\mathrm{Co^{2+}}][\mathrm{O_2}][\mathrm{HAAH}]^{1/2} \qquad (\mathrm{b}\cdot 2)$$

iii) By assuming $\mathrm{d}[\mathrm{HAAO_2\cdot}]/\mathrm{d}t = 0$ and $\mathrm{d}[\{\mathrm{Co^{2+}}\text{-}(\mathrm{AAH^-})_2\}\cdots\mathrm{O_2}]/\mathrm{d}t = 0$* in the reaction 5, Eq. c·1 is obtained:

$$k_5[\{\mathrm{Co^{2+}(AAH^-)_2}\}\cdots\mathrm{O_2}][\mathrm{HAAO_2\cdot}] = K_{\mathrm{c}} \qquad (\mathrm{c}\cdot 1)$$

By introducing $[\{\mathrm{Co^{2+}(AAH^-)_2}\}\cdots\mathrm{O_2}] = K_1^2\cdot K_{\mathrm{m}}^2\cdot K_{\mathrm{a}}^2\cdot[\mathrm{Co^{2+}}]^2[\mathrm{HAAH}]^2[\mathrm{O_2}]$ into Eq. c·1, Eqs. c·2 and c·3 are obtained:

$$k_5\cdot K_1^2\cdot K_{\mathrm{m}}^2\cdot K_{\mathrm{a}}^2[\mathrm{Co^{2+}}]^2[\mathrm{HAAH}]^2\cdot$$
$$[\mathrm{O_2}][\mathrm{HAAO_2\cdot}] = K_{\mathrm{c}} \qquad (\mathrm{c}\cdot 2)$$

Hence,

$$[\mathrm{HAAO_2\cdot}] = K_{\mathrm{c}}(k_5\cdot K_1^2\cdot K_{\mathrm{m}}^2\cdot K_{\mathrm{a}}^2)^{-1}\cdot$$
$$[\mathrm{Co^{2+}}]^{-2}[\mathrm{HAAH}]^{-2}[\mathrm{O_2}]^{-1} \qquad (\mathrm{c}\cdot 3)$$

By mutiplying c·3 by b·2, Eq. d is derived:

$$[\mathrm{HAAO_2\cdot}]^3 = \{(k_2\cdot K_{\mathrm{c}})/(k_5\cdot k_{10}\cdot K_1^2\cdot K_{\mathrm{m}}\cdot K_{\mathrm{a}}^{3/2})\}\cdot$$
$$[\mathrm{Co^{2+}}]^{-1}[\mathrm{HAAH}]^{-3/2}$$

hence:

$$[\mathrm{HAAO_2\cdot}] = \{(k_2\cdot K_{\mathrm{c}})/(k_5\cdot k_{10}\cdot K_1^2\cdot$$
$$K_{\mathrm{m}}\cdot K_{\mathrm{a}}^{3/2})\}^{1/3}[\mathrm{Co^{2+}}]^{-1/3}[\mathrm{HAAH}]^{1/2} \qquad (\mathrm{d})$$

By substituting d into a·2, Eq. e is obtained and rewritten as Eq. f:

$$-\mathrm{d}[\mathrm{O_2}]/\mathrm{d}t = k_4\{(k_2\cdot K_{\mathrm{c}})$$
$$/(k_5\cdot k_{10}\cdot K_1^2\cdot K_{\mathrm{m}}\cdot K_{\mathrm{a}}^{3/2})\}^{1/3}\cdot$$
$$[\mathrm{Co^{2+}}]^{-1/3}[\mathrm{HAAH}]^{1/2} \qquad (\mathrm{e})$$

or: $-\mathrm{d}[\mathrm{O_2}]/\mathrm{d}t = k_{\mathrm{a}}[\mathrm{Co^{2+}}]^{-1/3}[\mathrm{HAAH}]^{1/2}$ (f)

where $k_{\mathrm{a}} = k_4\{(k_2\cdot K_{\mathrm{c}})/(k_5\cdot k_{10}\cdot K_1^2\cdot K_{\mathrm{m}}\cdot K_{\mathrm{a}}^{3/2})\}^{1/3}$.

In the Case of $[\mathrm{HAAH}]/[\mathrm{Co^{2+}}] \geq 4$:

It is assumed that the chain reaction proceeds by way of Eqs. 11—19:

Initiation

$$\mathrm{Co^{2+}} + \mathrm{O_2} \underset{k_{-11}}{\overset{k_{11}}{\rightleftarrows}} \mathrm{Co^{2+}\cdots O_2}^{6)} \ (\text{or } \mathrm{Co^{3+}\cdots O_2^-})^{6)} \qquad V_{11},\ V_{-11} \quad (11)$$

$$\mathrm{Co^{2+}\cdots O_2} + \mathrm{HAAH} \xrightarrow{k_{12}} \mathrm{Co^{2+}} + \mathrm{HAA\cdot} + \mathrm{HO_2\cdot} \qquad V_{12} \quad (12)$$

Propagation

$$\mathrm{HAA\cdot} + \mathrm{O_2} \xrightarrow{k_{13}} \mathrm{HAAO_2\cdot} \qquad V_{13} \quad (13)$$

$$\mathrm{HAAO_2\cdot} + \mathrm{HAAH} \xrightarrow{k_{14}} \mathrm{HAAO_2H} + \mathrm{HAA\cdot} \qquad V_{14} \quad (14)$$

Branched propagation

$$\mathrm{Co^{2+}(AAH^-)_2} + \mathrm{HAAO_2H} \xrightarrow{k_{15}} \{\mathrm{Co^{3+}}\text{-}(\mathrm{AAH^-})_2\}^+ + \mathrm{HAAO\cdot} + \mathrm{OH^-} \qquad V_{15} \quad (15)$$

$$\{\mathrm{Co^{3+}(AAH^-)_2}\}^+ + \mathrm{HAAH} \xrightarrow{k_{16}} \mathrm{Co^{2+}(AAH^-)_2} + \mathrm{HAA\cdot} + \mathrm{H^+} \qquad V_{16} \quad (16)$$

$$\mathrm{HAAO\cdot} + \mathrm{HAAH} \xrightarrow{k_{17}} \mathrm{HAAOH} + \mathrm{HAA\cdot} \qquad V_{17} \quad (17)$$

Termination

$$2\mathrm{HAAO_2\cdot} \xrightarrow{k_{18}} \text{Inactive products} \qquad V_{18} \quad (18)$$

$$\mathrm{Co^{3+}(AAH^-)_2O_2^-} + \mathrm{HAA\cdot} \underset{k_{19}}{\overset{k_{19}}{\rightleftarrows}} \mathrm{Co^{3+}(AAH^-)_3} + \mathrm{O_2} \qquad V_{19},\ V_{-19} \quad (19)$$

In this case, the reaction is initiated by the action of cobaltous peroxide on HAAH, since the concentration of HAAH is higher than that in the preceding case, and the HAA· produced induces the propagation reaction. The hydroperoxide produced in the reaction 14 induces the branched propagation reaction. The reactions 18 and 19, in which the former belongs to the conventional self-termination while the latter belongs to the exchange reaction between the ligands, is supposed to be the termination stage. By assuming $V_{18} \gg V_{19}$ on the basis of the experimental conditions, the reaction 18 may be expected to be predominant in the termination stage. The reaction 19 is supposed to be reversible, since the solution was dark

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* The bridged compound, $\mathrm{(AAH^-)_2Co^{2+}\cdots O_2\cdots Co^{2+}(AAH^-)_2}$, is formed as follows:[4]

$$\mathrm{Co^{2+}(AAH^-)} + \mathrm{HAA\cdot}\ (\text{or } \mathrm{HAAO\cdot},\ \mathrm{HAAO_2\cdot}) \overset{K_{\mathrm{d}}}{\rightleftarrows} \mathrm{Co^{3+}(AAH^-)_2}$$

$$\mathrm{Co^{3+}(AAH^-)_2} + \mathrm{O_2} \overset{K_{\mathrm{e}}}{\rightleftarrows} \mathrm{Co^{3+}(AAH^-)_2O_2} \overset{K_{\mathrm{f}}}{\rightleftarrows} \mathrm{Co^{2+}(AAH^-)_2O_2\cdot}$$

$$2\mathrm{Co^{2+}(AAH^-)_2O_2\cdot} \overset{K_{\mathrm{g}}}{\rightleftarrows} \{\mathrm{Co^{2+}(AAH^-)_2}\}_2\cdots\mathrm{O_2} + \mathrm{O_2}$$

Hence:

$$K_{\mathrm{d}}\cdot K_{\mathrm{e}}\cdot K_{\mathrm{f}}\cdot K_{\mathrm{g}} = K$$
$$= [\{\mathrm{Co^{2+}(AAH^-)_2}\}\cdots\mathrm{O_2}]/[\mathrm{Co^{2+}(AAH^-)}]^2[\mathrm{HAA\cdot}]^2[\mathrm{O_2}]$$

Since HAA· (or HAAO·, $\mathrm{HAAO_2\cdot}$) is constant at a steady state and since $\mathrm{Co^{2+}}$ ($\mathrm{AAH^-}$) is approximately constant at $[\mathrm{HAAH}]/[\mathrm{Co^{2+}}] \leq 3$ on the basis of the Bjerrum's assumption,[5] the $\{\mathrm{Co^{2+}(AAH^-)_2}\}_2\cdots\mathrm{O_2}$ value is almost constant also. Since HAA· is formed through the reaction accompanying HAAH or $\mathrm{AAH^-}$, at a steady state it may be proportional to $[\mathrm{AAH^-}]$.

Therefore, $[\mathrm{HAA\cdot}] = K_1\cdot[\mathrm{AAH}]$, and:

$$K = [\{\mathrm{Co^{2+}(AAH^-)_2}\}_2\cdots\mathrm{O_2}]/$$
$$K_1^2\cdot K_{\mathrm{m}}^2\cdot[\mathrm{Co^{2+}}]^2[\mathrm{AAH^-}]^4[\mathrm{O_2}]^{-1}$$
$$= [\{\mathrm{Co^{2+}(AAH^-)_2}\}_2\cdots\mathrm{O_2}]/$$
$$K_1^2\cdot K_{\mathrm{m}}^2\cdot K_{\mathrm{a}}^2\ [\mathrm{Co^{2+}}]^2[\mathrm{HAAH}]^2[\mathrm{O_2}]^{-1}$$

4) Cf. E. M. Arnett and M. A. Mendelsohn, *J. Am. Chem. Soc.*, **84**, 3828 (1962).

5) J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Hasse Son, and Copenhagen (1941).

6) N. Uri, *Nature*, **177**, 1177 (1956); H. Hock and H. Kropf, *Angew. Chem.*, **69**, 313 (1957).

green even after the completion of the oxidation reaction, and green cobaltic chelates, $Co^{3+}(AAH^-)_3$, were extracted into the benzene layer. The absorption rate of oxygen is shown by Eq. A·1.

$$-d[O_2]/dt = V_{13} = k_{13}[HAA\cdot][O_2] \qquad (A\cdot 1)$$

i—iii below are assumed under a steady state.

i) By assuming $d[HAAO_2\cdot]/dt=0$, $V_{13}=V_{14}+V_{18}$. Since the chain is long enough and since $V_{prop.} \gg V_{term.}$, V_{13} is approximately equal to V_{14} and Eq. B is obtained:

$$k_{13}[HAA\cdot][O_2] = k_{14}[HAAO_2\cdot][HAAH] \qquad (B)$$

Therefore, A·1 is expressed by A·2:

$$-d[O_2]/dt \fallingdotseq V_{14}=k_{14}[HAAO_2\cdot][HAAH] \quad (A\cdot 2)$$

ii) The rate of the initiation reaction, $V_{init.}$, should be equal to the rate of the termination reaction, $V_{term.}$, in order that the propagation reaction may proceed under a steady state. Therefore, $k_{12}[Co^{2+}\cdots O_2][HAAH]=k_{18}[HAAO_2\cdot]^2$.

By introducing $k_{11}/k_{-11}=K_n$ and $[Co^{2+}\cdots O_2]=K_n[Co^{2+}][O_2]$, Eq. C·1 is obtained:

$$k_{12}\cdot K_n[Co^{2+}][O_2][HAAH]= k_{18}[HAAO_2\cdot]^2 \qquad (C\cdot 1)$$

By substituting $[AAH^-]=K_a^{1/2}[HAAH]^{1/2}$ into C·1, Eq. C·2 is obtained:

$$[HAAO_2\cdot]=(k_{12}\cdot K_n\cdot K_a/k_{18})^{1/2}\cdot [Co^{2+}]^{1/2}[O_2]^{1/2}[AAH^-] \qquad (C\cdot 2)$$

iii) By assuming $V_{19}/V_{-19}=K_h$, in which K_h is constant, Eq. D·1 is obtained:

$$K_h = (k_{19}[Co^{3+}(AAH^-)_2O_2^-][HAA\cdot]) /(k_{-19}[Co^{3+}(AAH^-)_3][O_2]) \qquad (D\cdot 1)$$

The cobaltic chelates are formed in accordance with the following reactions:

$$\{Co^{3+}(AAH^-)_2\}^+ + AAH^- \overset{Ki}{\rightleftarrows} Co^{3+}(AAH^-)_3$$

$$\{Co^{3+}(AAH^-)_2\}^+ + O_2^- \overset{Kj}{\rightleftarrows} Co^{3+}(AAH^-)_2\cdot O_2^-$$

By using these relations, Eq. D·1 may be rewritten as Eq. D·2:

$$[HAA\cdot] = (k_{-19}\cdot K_h\cdot K_i/k_{19}\cdot K_j)\cdot [AAH^-][O_2][O_2^-]^{-1} \qquad (D\cdot 2)$$

By combining B and D·2, Eq. E is obtained:

$$[HAAO_2\cdot]=(k_{13}\cdot k_{-19}\cdot K_h\cdot K_i/k_{14}\cdot k_{19}\cdot K_j\cdot K_a{}^{1/2})\cdot [AAH^-]^{-1}[O_2]^2[O_2^-]^{-1} \qquad (E)$$

By multiplying C·2 by E, Eq. F is obtained:

$$[HAAO_2\cdot]^2= (k_{12}\cdot K_n/k_{18})^{1/2}(k_{13}\cdot k_{-19}\cdot K_h\cdot K_i/k_{14}\cdot k_{19}\cdot K_j)\cdot [Co^{2+}]^{1/2}[O_2]^{5/2}[O_2^-]^{-1}$$

Hence:

$$[HAAO_2\cdot]= (k_{12}\cdot K_n/k_{18})^{1/4}(k_{13}\cdot k_{-19}\cdot K_h\cdot K_i/k_{14}\cdot k_{19}\cdot K_j)^{1/2}\cdot [Co^{2+}]^{1/4}[O_2]^{5/4}[O_2^-]^{-1/2} \qquad (F)$$

By substituting F into A·2, Eq. G is obtained:

$$-d[O_2]/dt= k_{14}(k_{12}\cdot K_n/k_{18})^{1/4}(k_{13}\cdot k_{-19}\cdot K_h\cdot K_i/k_{14}\cdot k_{19}\cdot K_j)^{1/2}\cdot [Co^{2+}]^{1/4}[HAAH][O_2]^{5/4}[O_2^-]^{-1/2} \qquad (G)$$

Since the oxygen pressure is definite and since the $[O_2^-]$ value is approximately constant under a steady state, G is expressed briefly by Eq. H:

$$-d[O_2]/dt = k_b[Co^{2+}]^{1/4}[HAAH] \qquad (H)$$

By taking the following equilibrium into consideration, Eq. 1 is obtained:

$$Co^{2+}(AAH^-)_2+O_2 \overset{K_p}{\rightleftarrows} Co^{2+}(AAH^-)_2\cdots O_2 \overset{K_q}{\rightleftarrows} Co^{3+}(AAH^-)_2\cdots O_2^- \overset{K_j{}^{-1}}{\rightleftarrows} \{Co^{3+}(AAH^-)_2\}^+ + O_2^- \qquad (20)$$

$$Co^{2+} + 2AAH^- \overset{K_s}{\rightleftarrows} Co^{2+}(AAH^-)_2, \text{ and}$$

$$Co^{3+} + 2AAH^- \overset{K_t}{\rightleftarrows} \{Co^{3+}(AAH^-)_2\}^+$$

$$[O_2^-]=\{(K_p\cdot K_q\cdot K_j{}^{-1}\cdot K_s)/K_t\}\cdot [O_2][Co^{2+}]/[Co^{3+}] \qquad (I)$$

Since the $[Co^{2+}]/[Co^{3+}]$ is considered to be approximately constant under a steady state, the $[O_2^-]$ may also be expected to be almost constant.

The Relationship among the Induction Period, [HAAH] and the Total Amount of Oxygen Absorbed.—The induction period is supposed to depend on the time interval in which the amount of HAA· necessary for the progress of the reaction 3 or 13 could be accumulated in the solution. In the reaction using a definite amount of Co^{2+}, the concentration of Co^{2+} decreases with an increase in the mole ratio of $[HAAH]/[Co^{2+}]$, since Co^{2+} is more or less consumed in the formation of the chelate. The induction period is, therefore, considered to become longer with an increase in the mole ratio of $[HAAH]/[Co^{2+}]$.

It may also be supposed, on the basis of the experimental results, that the liberated HAAH can be oxidized more easily than the chelated HAAH. When the amount of HAAH increases in proportion to a definite amount of cobalt, the increases in the liberated HAAH is not so large as the increase in the HAAH added, since some parts of HAAH are consumed in the formation of the chelate.

Therefore, the total amount of the oxygen absorbed is not considered to increase markedly in comparison with the increase in the [HAAH] added. In the case of $[HAAH]/[Co^{2+}]>3$, about one-half of the increment in the HAAH added is considered to take part in the chelate formation.

The Oxidation of *p*-Xylene and Toluene Using the Co-HAAH System.—At the beginning of the radical chain reaction, the formation of the radicals by withdrawing the hydrogen atom from the hydrocarbons is induced with tervarent cobalt,[1,7] including the metal peroxide.[6,8] Though the formation of Co^{3+} in an aqueous solution is not easy, since $E° = -1.84$ V., the cobalt in the activated state seems to be easily formed in glacial acetic acid in the presence of such ketones as ethyl methyl ketone, HAAH, acetonylacetone and ethyl acetoacetate.

It is easily ascertained spectroscopically that Co^{2+} is converted with oxygen into the higher valency state or the activated state in the presence of HAAH.

Therefore, the formation of the radicals from *p*-xylene and toluene seems to be reduced to the action of $HAAO_2\cdot$, Co^{3+} and $\{Co^{3+}(AAH^-)_2\}^+$, etc., against them. As is shown in Fig. 2, the absorption rate of oxygen in the presence of 0.5 mol./l. *p*-xylene is slower than that in the absence of *p*-xylene.

This shows that the active species produced in the solution might be consumed by reacting with *p*-xylene. However, the formation of the radical seems to be based on the action of Co^{3+} and $\{Co^{3+}(AAH^-)_2\}^+$, since the concentration of $HAAO_2\cdot$ is not as high as is necessary for Eq. 21 to hold:

$$RH + HAAO_2\cdot \rightarrow R\cdot + HAAO_2H \qquad (21)$$

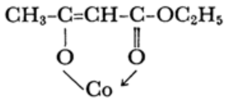
It is clear from Fig. 3 that the cobaltic acetylacetonate, $Co^{3+}(AAH^-)_3$, could be almost stable for the oxidation with oxygen. Though the co-existence of a suitable amount of HAAH is necessary for the oxidation of *p*-xylene and toluene, the formation of $Co^{3+}(AAH^-)_3$ becomes easier with an increase in the mole ratio of $[HAAH]/[Co^{2+}]$, while the formation of the activated species of Co^{2+} becomes more difficult with a decrease in the mole ratio of $[HAAH]/[Co^{2+}]$. Therefore, the optimum conditions for the oxidation of *p*-xylene and toluene are when $[HAAH]/[Co^{2+}]=2$.

In the cobaltous acetylacetonate, $Co^{2+}(AAH^-)_2$, four co-ordination positions are already occupied with AAH^-, but there are still two vacant positions which can be easily co-ordinated with water, acetic acid, oxygen molecules, etc.

In the case of a co-ordination with O_2 as is shown in the reaction 20, it is supposed that Co^{2+} and O_2 are converted into Co^{3+} and O_2^- respectively; these activated species make the withdrawing of hydrogen atoms from hydrocarbon easier. Since the ease of the formation of the negatively charged oxygen species are generally in the order of $O_2^- > O^- > O^{2-}$,[9] the oxygen in the activated species is assumed to be O_2^-.

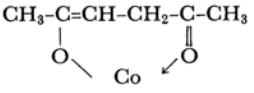
Since such ketones as ethyl acetoacetate and acetonylacetone show a smaller co-ordination ability to cobalt ions than HAAH, the cobalt chelates with these ligands are expected to be too unstable to resist oxidation.

When the authors write the structure of the chelate of the acetoacetic ester:

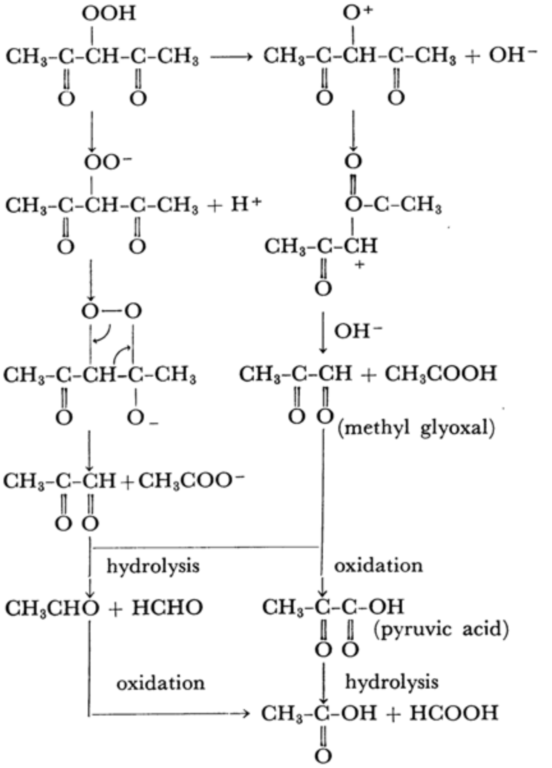

$CH_3\text{-}C{=}CH\text{-}C\text{-}OC_2H_5$

it may be seen that the enolate (or benzenoid) resonance involving the cobalt is greatly interferred with by the participation of one of the C=O groups in the very strong ester resonance, thus accounting for the very large decrease in the stability of the chelate.[10]

Since it is generally accepted that a six-membered chelate ring is much more stable than a seven-membered one,[11] the cobalt chelate of acetonlylacetone with a seven-membered ring is not expected to be more stable than that of HAAH with a six-membered ring.


$CH_3\text{-}C{=}CH\text{-}CH_2\text{-}C\text{-}CH_3$

Hence, the equilibrium concentrations of the unbound acetoacetic ester and acetonylacetone



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7) C. E. H. Bawn and J. E. Jolley, *Proc. Roy. Soc.*, **237**, 297 (1956), etc.

8) H. Kropf, *Ann.*, **637**, 73, 93, 111 (1960).

9) N. Ohta et al., "Shokubai Kōgaku Kōza (Catalytic Engineering)," Vol. 7, Catalysts Society of Japan, Chijinshokan & Co. Ltd., Tokyo (1964), p. 11.

10) M. Calvin and K. W. Wilson, *J. Am. Chem. Soc.*, **67**, 2007 (1945).

11) For example, D. P. Graddon, "An Introduction to Co-ordination Chemistry," Pergamon Press, Oxford (1961), Chap. 4.

are expected to be higher than that in HAAH.

It is, therefore, considered that the oxidation of hydrocarbons in the presence of the above ketones proceeds favorably even when the mole ratio is [ketone]/[Co^{2+}]=3.

Oxidation Products of Acetylacetone.— The oxidation products identified by gas chromatography are considered to come from $HAAO_2H$ or $HAAO_2\cdot$ by the mechanisms as show in page 671.

Summary

Acetylacetone is oxidized in a glacial acetic acid solution containing bi-valent cobalt to produce α-hydroperoxyacetylacetone, by which Co^{2+} is further oxidized to Co^{3+}.

At the end of the oxidation, acetylacetone is converted into formic acid, acetic acid, and small amounts of aldehydes.

Under a definite pressure of oxygen, the oxidation rates are as follows; at $[HAAH]/[Co^{2+}] \leq 3$,

$$-d[O_2]/dt = k_a[HAAH]^{1/2}[Co^{2+}]^{-1/3}$$

and at $[HAAH]/[Co^{2+}] \geq 4$,

$$-d[O_2]/dt = k_b[HAAH][Co^{2+}]^{1/4}$$

In order to oxidize toluene and *p*-xylene in the glacial acetic acid solution containing Co and HAAH catalysts, the formation of Co^{3+} and $\{Co^{3+}(AAH^-)_2\}^+$ in the solution is indispensable. Since the [HAAH] is insufficient for the formation of Co^{3+} at the mole ratio of $[HAAH]/[Co^{2+}] < 2$, and since the stable chelate, $Co^{3+}(AAH^-)_3$, is easily produced at the mole ratio of $[HAAH]/[Co^{2+}] > 3$, the Co-HAAH systems are considered to be active only at the mole ratio of $[HAAH]/[Co^{2+}]=2$ for the oxidation of *p*-xylene and toluene. However, such ketones as acetonylacetone and ethyl acetoacetate are still active at the mole ratio of $[ketone]/[Co^{2+}]=3$, since these ligands form less stable complexes than the complex with HAAH.

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12) W. Pritzkow, *Chem. Ber.*, 87, 1668 (1954); 88, 482 (1955).