# The Accelerated Reaction of 2,2-Diphenyl-1-picrylhydrazyl with Cupric 3-(1-Butenyl)-2,4-pentanedionate in Frozen Solutions and Its ESR Spectra[1)]

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(Received November 1, 1971)

The rate enhancements upon freezing in the reaction of 2,2-diphenyl-1-picrylhydrazyl (DPPH) with cupric 3-(1-butenyl)-2,4-pentanedionate (3-α-butenylacetylacetonate) were studied in benzene, dioxane, and cyclohexane. It was observed that the degree of the rate enhancements in frozen solutions varied remarkably with the kind of solvent. The order of the accelerating effect was as follows: benzene>dioxane>cyclohexane. Upon freezing, the hyperfine structure in the ESR spectra of DPPH collapsed into a single line, but the peak-to-peak line width ($\Delta H_{pp}$) changed appreciably with the solvents used. The order of the values of $\Delta H_{pp}$ was as follows: cyclohexane >dioxane>benzene. These results suggest that the enhancement of the rate in a frozen solution is due to the increased concentration of reactants in the liquid region existing among the crystalline solvents.

Metal acetylacetonate reacts with a stable free radical, 2,2-diphenyl-1-picrylhydrazyl (DPPH), to yield 2,2-diphenyl-1-picrylhydrazine (DPPH-H); the reaction gives first-order kinetics for each reactant.[2)] In an earlier paper,[3)] it has been reported that this reaction is remarkably accelerated when a benzene solution of the reactants is frozen. This study was undertaken in an attempt to elucidate the frozen effect in more detail.

$$\text{DPPH} + \text{Cu(R-acac)}_2 \xrightarrow{k} \text{DPPH-H} + \text{other product}$$

Enhanced rates in frozen solutions for the catalytic hydrolysis of the penicilline β-lactam and some other reactions have been reported, and several possible explanations have been offered for the frozen effect.[4–13)] Pincock *et al.* have reported that there are highly concentrated liquid regions among the crystalline solvents when a dilute solution containing two reactants is frozen and that the reaction between the two reactants might be markedly accelerated by the concentration effect.[4–9)] Grant *et al.* have described how the acceleration of the reaction in frozen solutions can be attributed to other effects, including the higher proton mobility, the imposition of a favorable positional orientation between reactants, the participation of the ice crystal surface as a replacement for a catalyst molecule, and the change in the dielectric constant of the reaction media upon freezing.[10–13)]

In the reaction of DPPH with cupric 3-α-butenylacetylacetonate, the rate of the reaction was observed to be remarkably accelerated in benzene, but not appreciably so in cyclohexane, when the solutions were frozen. This solvent effect on the frozen reaction was considered on the basis of the ESR spectra of DPPH in these frozen solvents.

## Experimental

*Materials.* DPPH and cupric 3-α-butenylacetylacetonate were prepared in the way shown in a preceding paper.[2)] The solvents were purified by the ordinary method and were distilled before use.

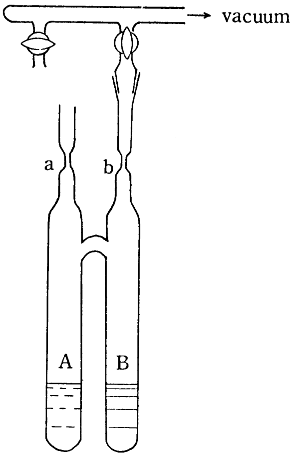

Fig. 1. Schematic drawing of the apparatus.

*Apparatus and Procedure.* The H-shaped tubes illustrated in Fig. 1 were used as the reaction cells. The solution of DPPH in A and the solution of the cupric chelate in B were simultaneously frozen in liquid nitrogen. The H-shaped tube was joined to a high-vacuum line after the tube had been sealed at the neck (a). Each solution was out-gassed by three freeze-thaw cycles under $10^{-5}$ mmHg, and then the H-shaped tube was sealed at (b). The solutions in A and B were warmed to room temperature and mixed thoroughly. The sealed tube was then immersed quickly into a dry ice–methanol mixture. The tube was allowed to remain submerged for a period of time to ensure complete freezing.

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*Kinetic Method.* The reaction was followed by the photometric measurement of the DPPH concentration using a EPS-3T Hitachi spectrometer. After having been removed from the dry ice–methanol bath, the reaction tube was placed in a methanol–water bath thermostated at the desired temperature. Upon warming to the temperature, the solutions remained solidly frozen. The tube was withdrawn from the bath after a certain lapse of time. To determine the concentration of DPPH, the frozen sample was melted at 25°C and the optical density of the solution at 525 mμ was measured as soon as possible after the tube was opened.

*ESR Spectra.* The ESR spectra of DPPH or cupric chelate in frozen solutions were recorded by means of a JES-3BX ESR spectrometer of Japan Electron Optics, using the X-band at the temperature of liquid nitrogen. Before measurement, the cubet containing the solution was immersed into a dry ice–methanol mixture for a period of time in a manner similar to that in the kinetic run.

## Results and Discussion

The effect of the solvent on the reaction rate in frozen solutions was studied. In Fig. 2, the plots of the reaction rate against the reaction temperature in a few solvents are shown. The rate has a maximum at −3°C for benzene (mp 5.5°C), at 8°C for dioxane (mp 11.7°C), and at 3°C for cyclohexane (mp 6.5°C). The maximum rates in these solvents appeared not at the freezing points of these solvents, but 3—9°C below them.

Pincock and Kiovsky[5–8] have also observed the appearance of the maximum rate several degrees below the freezing points of the solvents in some frozen systems and have explained it on the basis of the concentration effect. The maximum rate described above seems to result from a decrease in the rate constant and an increase in the concentration of the solute in the liquid region as the temperature is lowered.

The rate enhancement on freezing for a few solvents is shown in Table 1. The order of the rate enhancement is as follows:

benzene (24.1)>dioxane (5.39)>cyclohexane (2.42).

The values in parentheses show the ratio between the rate in the frozen solution at the temperature of the maximum rate and the rate determined by the extrapolation of the Arrhenius plot in liquid solutions to the

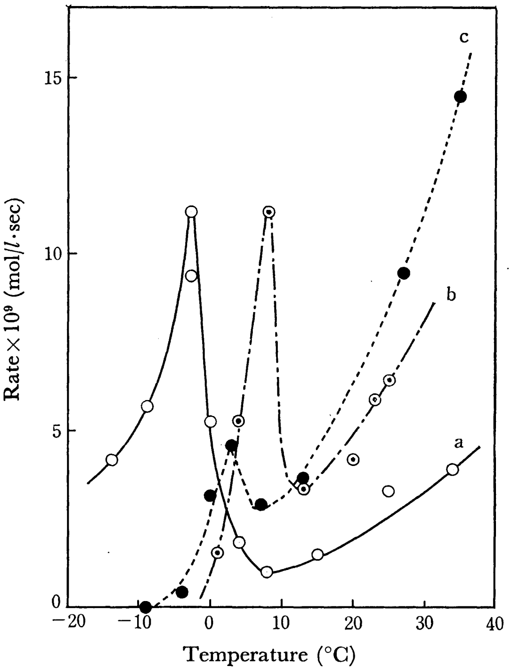


Fig. 2. Plots of rate *versus* temperature in a few solvents.
[DPPH] = $0.545 \times 10^{-4}$ mol/*l*,
[Cu(3-α-butenyl-acac)$_2$] = $4.68 \times 10^{-4}$ mol/*l*
a: benzene, b: dioxane, c: cyclohexane

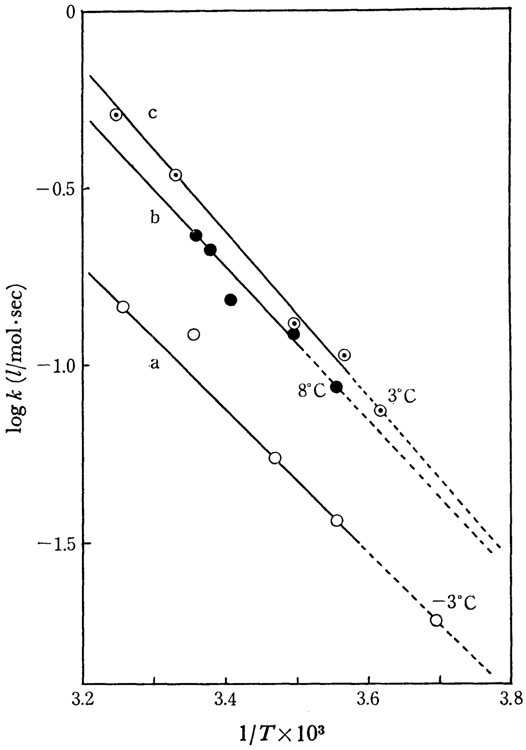


Fig. 3. Plots of log *k* *versus* 1/*T* in liquid solution.
[DPPH] = $0.545 \times 10^{-4}$ mol/*l*,
[Cu(3-α-butenyl-acac)$_2$] = $4.68 \times 10^{-4}$ mol/*l*
a: benzene, b: dioxane, c: cyclohexane

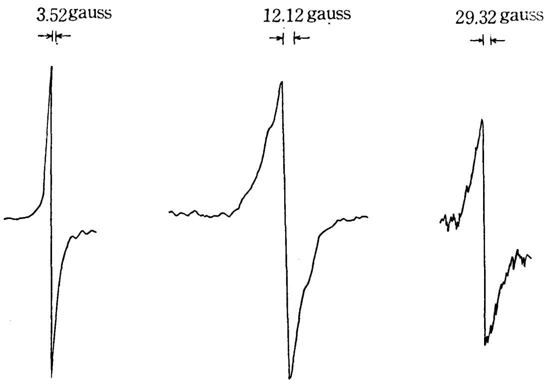
TABLE 1. THE EFFECTS OF THE SOLVENTS ON THE REACTIONS IN FROZEN SOLUTIONS
[DPPH] = $0.545 \times 10^{-4}$ mol/*l*, [Cu(3-α-butenyl-acac)$_2$] = $4.68 \times 10^{-4}$ mol/*l*

| Solvent | | | Temperature of maximum rate (°C) | Rate in frozen solution at the temp. of max. rate (× $10^9$mol/*l*•sec) | Rate in liquid solution extrapolated to the temp. of max. rate (× $10^9$mol/*l*•sec) | Rate ratio (frozen/liquid) |
|---|---|---|---|---|---|---|
| | Mp (°C) | $K_f$ | | | | |
| Benzene | 5.5 | 5.12 | −3 | 11.7 | 0.485 | 24.1 |
| Dioxane | 11.7 | 4.95 | 8 | 11.7 | 1.88 | 5.39 |
| Cyclohexane | 6.5 | 20.0 | 3 | 4.55 | 2.17 | 2.42 |

temperature of the maximum rate (Fig. 3).

Several recent papers have referred to the ESR spectra of DPPH and the spatial distribution of DPPH in frozen solutions. Roggin *et al.*[14] measured the ESR spectra of DPPH in a frozen benzene solution and reported that, upon freezing, the hyperfine structure of DPPH collapsed into a single line with a total width significantly less than that of the hyperfine spread and approximately equal to that observed for the concentrated polycrystalline DPPH. They have explained this phenomenon on the basis of the fact that DPPH is concentrated in small crystallites in which exchange interaction, which averages out the hyperfine structure, can occur. Ayscough *et al.*[15] studied the ESR spectra of deaerated frozen solutions of DPPH in various solvents and found that there were wide differences in line width, hyperfine splittings, and saturation behavior. They showed that the ESR spectra could be divided into three groups: (a) strong, exchange-narrowed line spectra (width from peak to peak, $\Delta H_{pp}=2$—4 gauss); (b) broader, unresolved line spectra ($\Delta H_{pp}=10$—20 gauss); (c) poorly resolved, five-line spectra. It has been explained that the spectra of group (b) result from some DPPH in the form of crystallites and some in a solid solution.

From these papers, it is clear that there is some correlation between the ESR spectra and the spatial distribution of DPPH in frozen solutions. Therefore, an investigation by means of the ESR spectra was carried out in order to obtain a possible explanation of the above solvent effects on the rate enhancements upon freezing.



Benzene Dioxane Cyclohexane

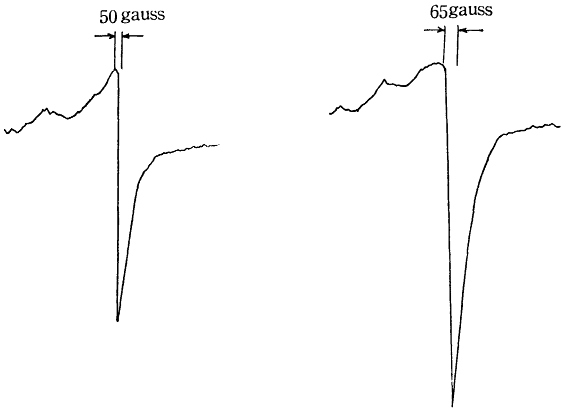
Fig. 4. ESR spectra of DPPH in the frozen solutions and peak to peak line width $\Delta H_{pp}$ (gauss).

The ESR spectra of DPPH in frozen solutions for the three solvents, benzene, dioxane, and cyclohexane, at the temperature of liquid nitrogen are shown in Fig. 4. The spectra in frozen benzene belonged to Group (a), as had been reported. On the other hand, the spectra in frozen dioxane and cyclohexane were found to belong to Group (b) in Ayscough's classification. The order of the magnitude of the $\Delta H_{pp}$ of DPPH in the frozen solution for the three solvents was as follows:

benzene (3.52 gauss)<dioxane (12.12 gauss)<cyclohexane (29.32 gauss).

The value of $\Delta H_{pp}$ in frozen benzene agreed with that of powder DPPH.[16] This proves that, in the benzene solution, DPPH is highly concentrated in small crystallites upon freezing. On the other hand, the value of $\Delta H_{pp}$ in frozen cyclohexane was remarkably large. This suggests that, in frozen cyclohexane solution, DPPH is scarcely concentrated at all in the form of crystallites and that almost all of the DPPH is in solid solution.

It was found that the $\Delta H_{pp}$ value of the ESR spectra in frozen solutions are closely related to the rate enhancement upon freezing in the reaction of DPPH with cupric 3-α-butenylacetylacetonate. That is, the smaller $\Delta H_{pp}$ value, the larger will be the rate enhancement upon freezing. This relationship between the $\Delta H_{pp}$ value and the rate enhancement suggests that the rate enhancement upon freezing in the reaction of DPPH with metal acetylacetonates is to be explained by the concentration effect mentioned by Pincock and Kiovsky.[5—8]



Benzene Cyclohexane

Fig. 5. ESR spectra of Cu(3-α-butenyl-acac)$_2$ in frozen solutions.

The ESR spectra of cupric 3-α-butenylacetylacetonate were also measured in a few frozen solutions, but they can not be discussed in detail. As is shown in Fig. 5, the $\Delta H_{pp}$ of the cupric chelate in a frozen benzene solution seems to be more narrow than that in frozen cyclohexane. Tominaga and Fujiwara[17] have reported that, in a frozen benzene solution containing 0.2M Co(acac)$_3$ at the temperature of dry ice, the most solute molecules are precipitated as microcrystals.

The facts presented above suggest that the reaction of DPPH with metal acetylacetonate in these frozen solutions is accelerated by the concentration of both reactants in the liquid region among the crystalline solvents upon freezing.

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