540 BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 45, 540—544 (1972) [Vol. 45, No. 2

The Reactions of Metal Acetylacetonates and Related Compounds with 2,2-Diphenyl-1-picrylhydrazyl[1]

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(Received June 18, 1971)

Some metal acetylacetonates ($M(acac)_n$) were observed to react with the stable free radical 2,2-diphenyl-1-picrylhydrazyl (DPPH) in organic solvents. For the reaction of cupric 3-α-butenylacetylacetonate with DPPH in benzene and cyclohexane, the following rate equation was obtained: $R=k$[cupric chelate][DPPH]. The activation parameters of the reaction were remarkably dependent upon the nature of the substituent and the metal atom in $M(acac)_n$, and upon the solvent. The results of the kinetic studies and the analytical work suggested that $M(acac)_n$ reacted with DPPH to yield 2,2-diphenyl-1-picrylhydrazine (DPPH-H) *via* the reduction of the central metal of the $M(acac)_n$.

In a previous communication,[2] it was reported that some metal acetylacetonates ($M(acac)_n$) reacted easily with 2,2-diphenyl-1-picrylhydrazyl (DPPH). The reaction will be described in more detail in this paper.

Although DPPH has been known as an efficient radical scavenger, it reacts with species other than radicals. For example, DPPH reacts with compounds having a labile hydrogen atom to produce a radical by the abstraction of the hydrogen atom.[3–13] Furthermore, DPPH also reacts with some metal salts to form redox systems or complexes.[14–18]

On the other hand, some $M(acac)_n$ are effective initiators of the radical polymerization of vinyl monomers.[19–22] To elucidate the reaction mechanism of $M(acac)_n$ with DPPH, we carried out kinetic studies and a determination of the products.

Experimental

Materials. The cupric 3-alkylacetylacetonates were prepared from an aqueous solution of cupric acetate and an ethanol solution of 3-alkylacetylacetone which has been synthesized from sodium salt of acetylacetone and alkyl bromide in the manner reported by Morgan and Martin.[23,24] The 3-α-butenylacetylacetone and other 3-α-alkenylacetylacetones were synthesized by the condensation of acetylacetone with *n*-butyraldehyde or other aldehydes in the presence of piperidine, according to the method shown in preceding papers.[21,25] Their cupric chelates were prepared from an aqueous solution of cupric acetate and an ethanol solution of 3-alkenylacetylacetone. The $Cu(acac)_2$, $Fe(acac)_3$, $Mn(acac)_3$, $Co(acac)_3$, $Zn(acac)_2$, $Al(acac)_3$, and $Cr(acac)_3$ were G.R.-grade reagents and were used without further purification. A G.R.-grade sample of DPPH was recrystallized from benzene-ligroin; mp 137—138°C. The solvents were purified by the ordinary method and were distilled before use.

Apparatus and Procedure. The reaction was followed by photometric measurements of the DPPH concentration using a Hitachi recording spectrophotometer, Model EPS-3T. For the reaction in air at atmospheric pressure, aliquots of the reaction mixture were pipetted out at regular intervals from the stock solution in a test tube thermostatted at 25°C. The absorbance of this solution at 525 mμ (in benzene) was measured. For the reaction under a vacuum (10^{-5} mmHg), the following procedure was employed throughout this investigation. The reaction mixture was degassed by the use of the H-shaped tube illustrated in Fig. 1 because the conventional freeze-thaw cycle was unsuitable for this study, as will be described in the next paper.[26] The solution of $M(acac)_n$ in A and the solution of DPPH in B were simultaneously frozen in liquid nitrogen, and the H-tube was joined to a high-vacuum line after the tube has been sealed at the (a) neck. Each solution was out-gassed by three freeze-thaw cycles under 10^{-5} mmHg, and then the H-tube was sealed at the (b) neck and separated from the vacuum line. The solutions in A and B were mixed thoroughly, and the resulting solution was transferred to the C section. The quartz cell, C, was immediately sealed at the (c) neck

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1) paper XIV in a series of "Catalytic Behavior of Metal Chelate Compounds".

2) K. Uehara, M. Tanaka, and N. Murata, This Bulletin, **41**, 3034 (1968).

3) K. E. Russell, *J. Phys. Chem.*, **58**, 437 (1954).

4) E. A. Braude, A. G. Brook, and R. P. Linstead, *J. Chem. Soc.*, **1954**, 3574.

5) J. C. Bevington, *ibid.*, **1956**, 1127.

6) J. E. Hazell and K. E. Russell, *Can. J. Chem.*, **36**, 1729 (1958).

7) J. C. McGowan, T. Powell, and R. Raw, *J. Chem. Soc.*, **1959**, 3103.

8) J. C. Hogg, D. H. Lohman, and K. E. Russell, *Can. J. Chem.*, **39**, 1588 (1961).

9) R. A. Bird, G. A. Harpell, and K. E. Russell, *ibid.*, **40**, 701 (1962).

10) P. J. Proll and L. H. Sutcliff, *Trans. Faraday Soc.*, **59**, 2090 (1962).

11) P. B. Ayscough and K. E. Russell, *Can. J. Chem.*, **43**, 3039 (1965).

12) S. Singh, K. R. Bhaskar, and C. N. R. Rao, *ibid.*, **44**, 2657 (1966).

13) P. B. Ayscough and K. E. Russell, *ibid.*, **45**, 3019 (1967).

14) L. H. Sutcliffe and J. Walkley, *Nature*, **178**, 999 (1956).

15) C. E. H. Bawn and D. Verdin, *Trans. Faraday Soc.*, **56**, 519 (1960).

16) R. I. Zusman, *Kinet. Katal.*, **7**, 414 (1966).

17) V. V. Voevodskii, R. I. Zusman, G. I. Shamovskaya, and Yu. N. Molin, *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk*, **1968**, 127. (*Chem. Abstr.*, **70**, 41190 (1969)).

18) H. Imai, Y. Ono, and T. Keii, *J. Phys. Chem.*, **72**, 46 (1968).

19) E. G. Kastning, H. Naarmann, H. Reis, and C. H. Berding, *Angew. Chem.*, **77**, 313 (1965).

20) C. H. Bamford and D. J. Lind, *Chem. Ind.* (London), **1965**, 1627.

21) K. Uehara, T. Matsumura, T. Nishi, F. Tamura, and N. Murata, *Kogyo Kagaku Zasshi*, **69**, 2027 (1966).

22) T. Otsu, N. Minamii, and Y. Nishikawa, *J. Makromol. Sci-Chem.*, **A2**, 905 (1968).

23) G. T. Morgan and A. E. Rawson, *J. Soc. Chem. Ind.*, **44**, 462 (1925). (*Chem. Abstr.*, **20**, 192 (1926)).

24) D. F. Martin, W. C. Fernelius, and M. Shamma, *J. Amer. Chem. Soc.*, **81**, 130 (1959).

25) K. Uehara, T. Matsumura, Y. Murata, M. Tanaka, and N. Murata, *Kogyo Kagaku Zasshi*, **72**, 1825 (1969).

26) K. Uehara, K. Kamei, M. Tanaka, and N. Murata, This Bulletin, *in press*.

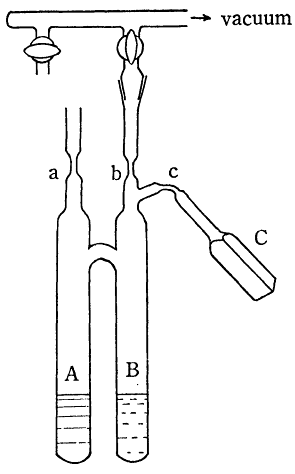

Fig. 1. Schematic drawing of the apparatus.

and separated from the H-tube. It was placed in the cell holder thermostatted at the desired temperature, and the optical density at 525 mμ was measured continuously.

The infrared spectra of the reaction products were measured on KBr disks by means of a Hitachi Model EPI-S2 infrared spectrometer. The mass spectra were recorded on a Hitachi Model RMU-6E mass spectrometer under the following conditions: ionization energy, 15 eV; total emission current, 80 μA; vacuum, 2×10^{-6} mmHg; sample temp., 250°C. The ESR spectra of cupric chelate in the presence of DPPH were measured by means of a Hitachi Model MES-4001 ESR spectrometer.

The isolation of products from the reaction mixture was carried out in the following way. Cupric 3-α-butenylacetylacetonate 1.2 g (0.0033 mol) was allowed to react with DPPH 0.87 g (0.0022 mol) in benzene under a vacuum for 48 hr. After the evaporation of the benzene, the cupric ion and 3-α-butenylacetylacetone were separated by twice extracting the resulting reaction mixture with 200 ml of disodium ethylenediaminetetraacetate (EDTA-2Na) on a hot plate. The residue after the extraction was a viscous brownish-red oil. By the recrystallization of the residue from methanol-water, an orange-brown powder (P) was obtained.

Results and Discussion

Most of the present studies were performed on cupric 3-α-butenylacetylacetonate because it has an appreciable solubility in nonpolar solvents and a high reactivity toward DPPH. Furthermore, this chelate is easily made and has been fairly well studied in our preceding papers.[25,27]

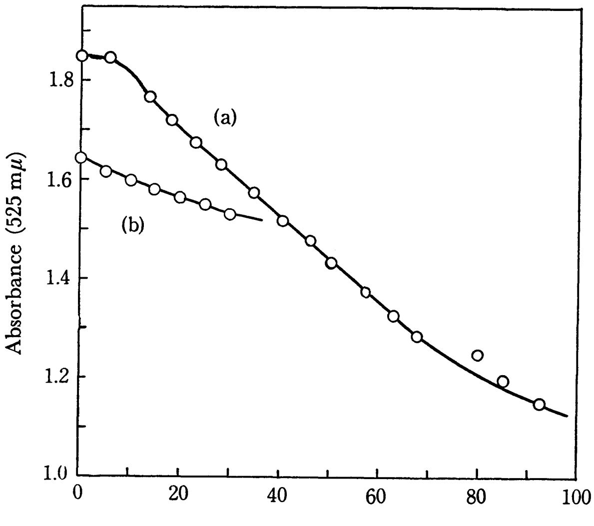

Fig. 2. The change of absorbance in the reaction of cupric 3-α-butenylacetylacetonate with DPPH at 25°C.
(a) in air, [cupric chelate] = 1.40×10^{-4} mol/l [DPPH] = 1.85×10^{-4} mol/l
(b) *in vacuo*, [cupric chelate] = 4.68×10^{-4} mol/l [DPPH] = 1.64×10^{-4} mol/l

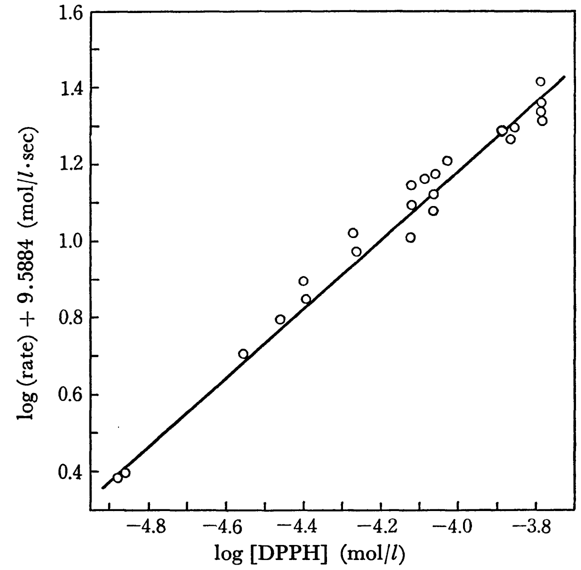

Fig. 3. Plot of log (rate) *versus* log [DPPH].
[Cu(3-α-butenyl-acac)$_2$] = 4.68×10^{-4} mol/l, 25°C.

The effects of oxygen on the reaction of cupric 3-α-butenylacetylacetonate with DPPH in benzene are summarized in Table 1. The rate of the reaction in atmospheric air was about 10 times that *in vacuo* (10^{-5} mmHg). Fig. 2 shows examples of the time-conversion relation for this reaction. A sigmoid curve was obtained in atmospheric air. The ap-

Table 1. The effects of air on the reaction of cupric 3-α-butenylacetylacetonate with DPPH
(At 25°C, in benzene, [DPPH] = 1.4×10^{-4} mol/l)

Atmosphere	[Cupric chelate] $\times10^4$ mol/l	Rate $\times10^8$ mol/l·sec	Activation energy kcal/mol	Kintic order DPPH	Cu
Vacuo (10^{-5} mmHg)	2.31	0.20	9.2	0.9	1.0
Air	1.40	1.47	11.1	1.6	1.4

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[27] K. Uehara, Y. Kataoka, K. Kamei, M. Tanaka, and N. Murata, *Kogyo Kagaku Zasshi*, **72**, 1831 (1969).

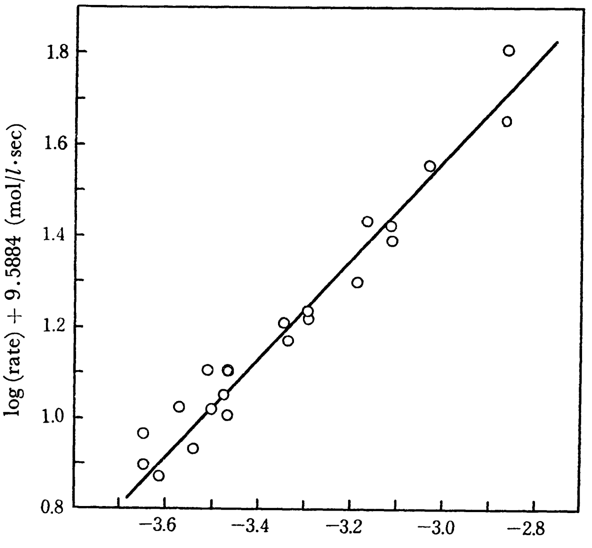


Fig. 4. Plot of log (rate) *versus* log [Cu(3-α-butenyl-acac)$_2$] at 25°C.
[DPPH] = 5.85×10^{-5} mol/*l*

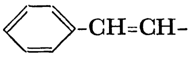
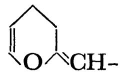
parent activation energy for the reaction was 9.2 kcal/mol *in vacuo* and 11.1 kcal/mol in atmospheric air. The relationships between the reaction rates and the initial concentrations of DPPH for a constant initial cupric chelate concentration *in vacuo* are shown in Fig. 3, from which the rate is found to increase with a 0.9 power[28] of the DPPH concentration. The dependencies of the rate of the reaction *in vacuo* on the concentration of the cupric chelate are shown in Fig. 4, from which the reaction rate is found to be first order with respect to the cupric chelate. In atmospheric air, the rate of the reaction (estimated from the portion of the initial straight line of the sigmoid curve) depended on the 1.4 power of the cupric chelate concentration and the 1.6 power of DPPH. These effects of air suggested that, in atmospheric air, oxygen virtually takes part in the reaction and complicates it. Therefore, to exclude the effect of oxygen, all subsequent experiments were carried out *in vacuo* (10^{-5} mmHg).

The solvent effects on this reaction are summarized in Table 2. In a few solvents the maxima of the absorption spectra of DPPH shifted to shorter wavelengths in the following order: benzene (525 mμ), dioxane (520 mμ), cyclohexane (513 mμ). It was found that the rate of the reaction in these solvents increased with a decrease in the λ_{max} of DPPH. The complex formation of DPPH with several solvents has been confirmed by means of elemental analysis[29] or X-ray diffraction data.[30] Recently, some investigators have reported that the formation of a charge-transfer complex between DPPH and benzene or dioxane was observed from the ESR spectra.[31,32] The solvent effect in the present reaction may be related in some way to the complex formation with these solvents.

TABLE 2. SOLVENT EFFECTS OF THE REACTION OF CUPRIC 3-α-BUTENYLACETYLACETONATE WITH DPPH
(*In vacuo*, [cupric chelate] = 4.68×10^{-4} mol/*l*, [DPPH] = 0.545×10^{-4} mol/*l*)

Solvent	Rate at 25°C mol/*l*·sec	Activation energy kcal/mol	Frequency factor *l*/mol·sec	λ_{max} of DPPH mμ	Kinetic order DPPH	Cu
Benzene	3.2×10^{-9}	9.2	7.0×10^{5}	525	0.9	1.0
Dioxane	6.4×10^{-9}	9.8	3.8×10^{6}	520	—	—
Cyclohexane	8.8×10^{-9}	10.6	2.0×10^{7}	513	1.0	1.0

TABLE 3. EFFECTS OF SUBSTITUENTS ON THE REACTION OF DPPH WITH Cu(3-R-acac)$_2$ IN BENZENE
([DPPH] = 0.545×10^{-4} mol/*l*, [Cu(3-R-acac)$_2$] = 4.68×10^{-4} mol/*l*)

No	R	Rate at 25°C mol/*l*·sec	Activation energy kcal/mol	Frequency factor *l*/mol·sec	Decomposition rate of the chelate in the polymerization of styrene at 70°C mol/*l*·sec
I		1.4×10^{-8}	9.0	2.2×10^{6}	3.3×10^{-7}
II		2.7×10^{-9}	—	—	—
III	$CH_3CH{=}CH-$	3.3×10^{-9}	8.9	4.3×10^{5}	—
IV	EtCH=CH-	3.1×10^{-9}	9.2	6.9×10^{5}	2.4×10^{-8}
V	CH_3-	1.0×10^{-11}	21.8	4.9×10^{12}	1.9×10^{-9}
VI	H-	$<10^{-11}$	—	—	—

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[28] The 0.6 power of the DPPH concentration in the preceding communication[2] is a typographical error and must be corrected to a 0.9 power.

[29] J. A. Lyons, W. F. Watson, *J. Polym. Sci.*, **18**, 141 (1955).

[30] D. E. Williams, *J. Amer. Chem. Soc.*, **88**, 5665 (1966), *ibid.*, **89**, 4280 (1967).

[31] R. Z. Sagdeev, *Zh. Strukt. Khim.*, **7**, 38 (1966). (*Chem. Abstr.*, **64**, 18733 (1966)).

[32] Yu. M. Ryzhmanov and A. A. Egorova, *Dokl. Akad. Nauk SSSR*, **191**, 148 (1970). (*Chem. Abstr.*, **73**, 20337 (1970)).

While the activation energies of this reaction increase in the order: benzene<dioxane<cyclohexane, the frequency factors markedly increase in the same order. The net reaction rates observed reflect the fact that the unfavorable activation energies are more than compensated for by the higher frequency factors.

First-order kinetics for each reactant were observed in benzene and cyclohexane. Sutcliffe and Walkly[14] have also pointed out that the redox reaction of metal acetate with DPPH in acetic acid gives first-order kinetics for each reactant and that the rate is reduced by the addition of benzene.

The effects of the replacement of the hydrogen atom in the 3-position of acetylacetone are shown in Table 3. The styryl derivative, I, showing the largest rate among the derivatives studied here had the same activation energy as III or IV, but a much higher frequency factor. It has been reported that the type of substituent markedly affects the frequency factor rather than the activation energy in the radical polymerization of styrene.[25,33]

The effects of metal atoms of metal acetylacetonates on the reaction rate are shown in Table 4. The order of the reactivity of $\mathrm{M(acac)}_n$ was as follows:

$$\mathrm{Mn(III)} > \mathrm{Fe(III)} > \mathrm{Zn(II)} > \mathrm{Co(III)} > \mathrm{Cu(II)},\ \mathrm{Al(III)},\ \mathrm{Cr(III)}$$

The observed reactivity order of $\mathrm{M(acac)}_n$ was independent of their stability constants (in water) and of the ionization potentials or electronegativities of their central metals, as was pointed out in connection with the radical polymerization initiated by $\mathrm{M(acac)}_n$.[22] The Mn(III) chelate was most reactive toward DPPH, which is in agreement with the activity in the radical polymerization of styrene[19] and methyl methacrylate.[22] On the other hand, the Co(III) chelate, which has a fairly high activity for the radical polymerization, was less reactive to DPPH. The lower reaction rate of $\mathrm{Co(acac)_3}$ is attributable to its lower frequency factor.

TABLE 4. THE REACTION OF DPPH WITH $\mathrm{M(acac)}_n$ IN BENZENE
($[\mathrm{DPPH}]=0.545\times10^{-4}\,\mathrm{mol}/l$, $[\mathrm{M(acac)}_n]=4.68\times10^{-4}\,\mathrm{mol}/l$)

$\mathrm{M(acac)}_n$	Rete at 25°C mol/l·sec	Activation energy kcal/mol	Frequency factor l/mol·sec
$\mathrm{Mn(acac)_3}$	9.8×10^{-10}	8.6	9.8×10^{4}
$\mathrm{Fe(acac)_3}$	2.2×10^{-10}	15.3	1.4×10^{9}
$\mathrm{Zn(acac)_2}$	1.9×10^{-10}	13.0	2.6×10^{7}
$\mathrm{Co(acac)_3}$	0.9×10^{-10}	6.5	2.1×10^{2}
$\mathrm{Cu(acac)_2}$	$<10^{-11}$	—	—
$\mathrm{Al(acac)_3}$	$<10^{-11}$	—	—
$\mathrm{Cr(acac)_3}$	$<10^{-11}$	—	—

The effects of solvents, substituents, and central metals showed that the reactivity of $\mathrm{M(acac)}_n$ toward DPPH could not be explained only by the activation energy. The difference between the frequency factors, especially the low frequency factor, is noteworthy.

The ESR spectra of cupric 3-α-butenylacetylacetonate in benzene in the presence of DPPH are shown in Fig. 5. The reduction of the central metal, Cu(II)→Cu(I), is established from the decrease in the intensity of the ESR spectra of Cu(II) with the time.

In order to identify the reaction product (P) isolated by the way described in the Experimental section, the following analyses were carried out. The infrared and ultraviolet absorption spectra of the product (P) agreed with those of an authentic sample of 2,2-diphenyl-1-picrylhydrazine(DPPH-H). The mass spectrum of (P) was closely analogous to that of DPPH-H. It showed the base peak at *m/e* 168 corresponding to that of (Ar-NH-Ar)$^+$, *m/e* 212 (picryl)$^+$ and *m/e* 227 (picryl-NH)$^+$. The value of the elemental analysis of this product also agreed with that of DPPH-H. Found: C, 54.70; H, 3.28; N, 17.28%. Calcd for $\mathrm{C_{18}H_{13}O_6N_5}$: C, 54.68; H, 3.28; N, 17.71%.

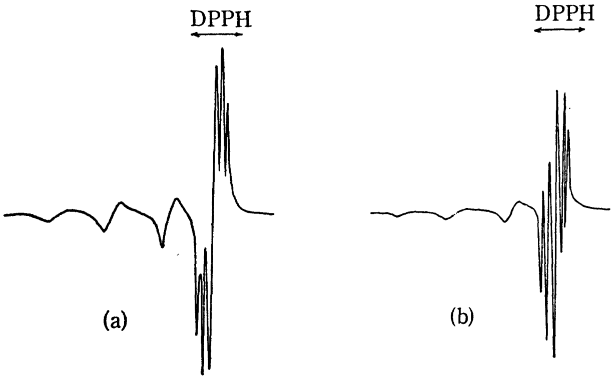
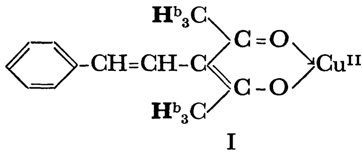


Fig. 5. ESR spectra of $\mathrm{Cu(3\text{-}\alpha\text{-butenyl\text{-}acac)_2}}$ in benzene in the presence of DPPH at room temperature.
(a) $t=0$ min (b) $t=60$ min

Cupric 3-α-butenylacetylacetonate has two kinds of labile hydrogen atoms ($\mathrm{H^a}$, $\mathrm{H^b}$). In order to investigate which kind of hydrogen atom takes part in the reaction, the reaction rate of the styryl derivative I, which has no labile $\mathrm{H^a}$ was compared with that of the butenyl derivative IV (Table 3). The I derivative showed a higher reactivity than the IV derivative toward DPPH, and the product in this reaction was also DPPH-H. This fact suggests that $\mathrm{H^a}$ does not take part in the reaction. Gritter and Ratmore[34] have shown in a study of the site of attack with a *t*-butoxy radical,[34] that a hydrogen atom is abstracted from the 1-position of metal acetylacetonate (H^b). Therefore, it is plausible that labile $\mathrm{H^b}$ was abstracted by DPPH in the reaction.



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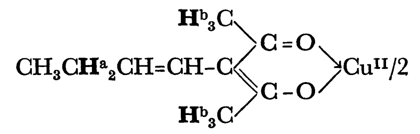
[33] C. H. Bamford and D. J. Lind, *Proc. Roy. Soc.*, **A302**, 145 (1968).

[34] R. J. Gritter and E. L. Ratmore, *Proc. Chem. Soc.*, **1962**, 328.



II

Therefore, 3-α-butenylacetylacetone (ligand) was used in place of its cupric chelate in the reaction with DPPH (Table 5). It was found that the reaction rate is one order of magnitude smaller than that for its cupric chelate.

TABLE 5. THE REACTION OF DPPH WITH 3-α-BUTENYL-ACETYLACETONE (LIGAND)

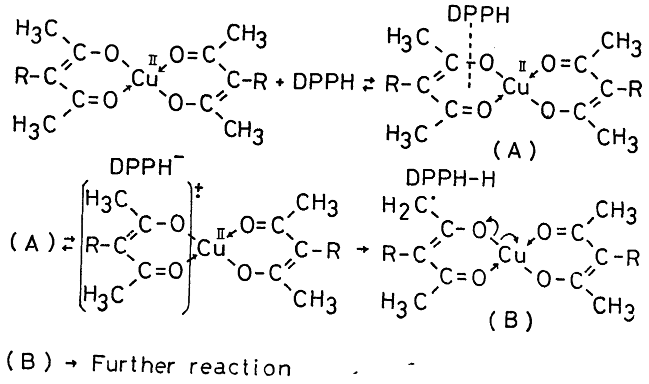
([3-α-butenylacetylacetone] $=4.68\times10^{-4}$ mol/*l*
[Cu(3-α-butenyl-acac)$_2$] $=4.68\times10^{-4}$ mol/*l*
[DPPH] $=0.545\times10^{-4}$ mol/*l*)

Reactant	Rate at 25°C mol/*l*·sec
3-α-butenylacetylacetone	0.35×10^{-9}
Cu(3-α-butenyl-acac)$_2$	3.1×10^{-9}

This lower reactivity of the ligand suggests that the electron transfer from the ligand to the central metal contributes to the reactivity of metal chelates.

As has been described in the Introduction, DPPH forms complexes with several kinds of organic solvents or metal salts. Therefore, it is probable that, in this reaction, the complex formation with M(acac)$_n$ promotes the internal electron transfer from the ligand to the central metal in the same manner as has been described for the system of Cu(acac)$_2$ and tetracyanoethylene.[35] This reaction involves the reduction of the central metal, but does not involve the oxidation of the metallic ion, as has been reported by Bawn and Verdin in the reaction of the ferrous ion and DPPH.[15] Furthermore, the complex formation is considered to lead DPPH to a favorable steric arrangement to abstract a hydrogen atom of the cupric chelate.

A possible mechanism embodying these ideas may be proposed for the reaction of M(acac)$_n$ with DPPH.



The mechanism is consistent with the observed kinetic results *in vacuo* and the products of the reaction. The internal electron transfer from the ligand to the central metal will facilitate the expulsion of a proton from a methyl group of metal acetylacetonate. The highest reactivity of cupric 3-styrylacetylacetonate (I) seems to result from phenyl group conjugated to the chelate ring, which would be expected to facilitate the internal electron transfer.[25]

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[35] K. Uehara, Y. Kataoka, M. Tanaka, and N. Murata, *Kogyo Kagaku Zasshi*, **73**, 1053 (1970).