The Reaction of Copper(II) Acetylacetonates with 2,2-Diphenyl-1-picrylhydrazyl in Benzene

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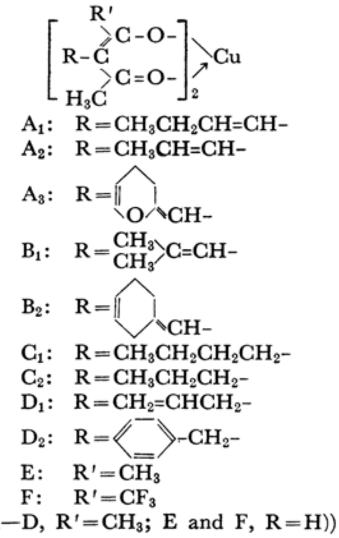
Sutcliffe and Walkley¹⁾ have pointed out that the redox reaction of metal acetate with 2,2-diphenyl-1-picrylhydrazyl (DPPH) in anhydrous acetic acid gives first-order kinetics for each reactant and that the rate is reduced by the addition of benzene.

This communication relates to a novel reaction of DPPH with metal complexes. Copper(II) acetylacetonates were allowed to react with DPPH in benzene at various temperatures. It was observed that as the reaction proceeded the absorption of DPPH at 525 mμ disappeared and that the reaction was accelerated by the presence of air. Furthermore, the rate was enormously enhanced in a frozen solution. In the experiments to be described below, the reaction mixture was degassed by a modified method because the conventional freeze-thaw cycle was unsuitable for this study.

The rate of the reaction varied remarkably with the structure of the ligand. As is shown in Table 1, the order of the reactivity of the copper(II) chelates was as follows:

$$A > B \gg C > D \gg E \gg F(\text{no reaction})$$

The order is essentially the same as that of the activity in the radical polymerization of styrene and the degree of extension of the ultraviolet tail of the copper(II) chelates²⁾ into the visible region.



(A—D, R'=CH_3; E and F, R=H))

TABLE 1. RATE DATA OF THE REACTION OF DPPH WITH Cu(II) CHELATES IN BENZENE

Cu(II)	Chelate (mol/l) $\times 10^4$	DPPH (mol/l) $\times 10^4$	Temperature (°C)	Rate (mol/l sec) $\times 10^9$
A_1	0.5	0.6	25	2.5
A_2	0.5	0.6	25	3.8
A_3	0.5	0.6	25	1.6
B_1	0.5	0.6	25	1.3
B_2	0.5	0.6	25	0.5
C_1	0.5	0.6	25	0.0
C_2	0.5	0.6	25	0.0
D_1	0.5	0.6	25	0.0
D_2	0.5	0.6	25	0.0
E	0.5	0.6	25	0.0
F	0.5	0.6	25	0.0
B_2	0.5	0.6	50	4.4
C_1	0.5	0.6	50	0.0
C_1	10.0	0.6	70	2.6
C_2	10.0	0.6	70	2.3
D_1	10.0	0.6	70	1.1
D_2	10.0	0.6	70	1.3
E	10.0	0.6	70	0.2
F	10.0	0.6	70	0.0
None	—	0.6	70	0.0
A_1	1.4	1.4	10	5.4
A_1	1.4	1.4	3[a]	19.5

[a] Frozen benzene solution.

In a frozen benzene solution (3°C), the rate of the reaction was enormously enhanced. A similar acceleration of rate was also observed in frozen *p*-dioxane and *p*-xylene.

The kinetic studies of this reaction were carried out with Cu(II) chelate A_1 in the range from 10 to 30°C. 0.6-order kinetics for DPPH and first-order kinetics for the Cu(II) chelate were observed. The activation energy of the reaction in the liquid benzene was 7.5 kcal/mol. The rate was reduced by the addition of 2,2-diphenyl-1-picrylhydrazine (DPPH-H), but increased by the addition of pyridine.

Mn(acac)$_3$, which is an effective initiator of the radical polymerization,³⁾ also reacts with DPPH in benzene and shows an enhanced rate in a frozen solution.

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

2) K. Uehara, M. Tanaka and N. Murata, This Bulletin, **41**, 3029 (1968).

3) C. H. Bamford and D. J. Lind, *Proc. Roy. Soc.*, **302**A, 145, (1968).