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On the Reactivity of Chlorine Atoms towards Alcohols

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Pulse radiolysis has been used to determine reaction rate constants of chlorine atoms with various alcohols in carbon tetrachloride solutions by competition kinetic methods taking the absorption of the complex formed in the reaction of dimethyl sulfoxide and chlorine atoms as a reference system.

Alcohols are known as an effective scavenger of chlorine atoms,[1)] and are added as a stabilizer to commercial chloroform. However, the rate constant reported hitherto has been estimated from the conductometric measurement with a large uncertainty.[2)] In a previous paper,[3)] the novel transient absorption with a peak at 400 nm produced on a 10 ns electron pulse irradiation of dimethyl sulfoxide (DMSO) in carbon tetrachloride has been assigned to complexes of DMSO and a chlorine atom (Eq. 1). We applied the competition method to determine bimolecular rate constants for reactions of chlorine atoms with 9 alcohols (Eq. 2) taking the absorption of this complex as a reference system.

$$\mathrm{DMSO + Cl \xrightarrow{k_1} (DMSO{\cdot}Cl)} \qquad (1)$$

$$\mathrm{ROH + Cl \xrightarrow{k_2} ROH(-H) + HCl} \qquad (2)$$

Figure 1 shows apparent first order rate constants of grow-in of the 400 nm band as a function of DMSO concentration. A good straight line obtained suggests that the rate constant k_{obsd} can be expressed by Eq. 3. The reaction rate constant of

$$k_{obsd} = k_0 + k_1[\mathrm{DMSO}] \qquad (3)$$

DMSO and chlorine atoms and the half lifetime of chlorine atoms in CCl_4 are calculated to be $(7.0 \pm 0.5) \times 10^9$ $\mathrm{mol^{-1}\ dm^3\ s^{-1}}$ and 140 ns, respectively. Chlorine atoms abstract hydrogen atoms from alcohols and provided that the product of reaction 2 dose not absorb at 400 nm, then the competition between Eqs. 1 and 2 can be represented

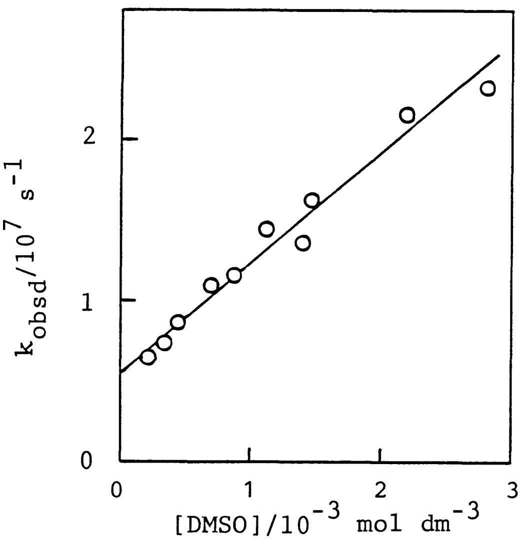

Fig. 1. Apparent first order rate constants of the formation of (DMSO·Cl) complexes at 18 °C. Absorbed dose: 135 Gy.

by Eq. 4, where OD_0 and OD denote the optical density of the 400 nm band in the absence and presence of alcohols.

$$OD_0/OD = 1 + k_2[ROH]/k_1[DMSO] \qquad (4)$$

Chlorine atoms were produced on pulse irradiation of argon saturated carbon tetrachloride solutions containing 2.8×10^{-3} mol dm^{-3} DMSO and a various amount of alcohols. Figure 2 shows the ratio OD_0/OD as a function of alcohol concentration. Straight lines are obtained for each alcohol under investigation. Second order reaction rate constants thus obtained are summarized in Table 1.

It is noted that the reactivity of alcohols towards chlorine atoms depends on the structure of them rather than the molecular size. Alcohols which have a chain containing more than two carbon atoms from the hydroxy group such as n-C_3H_7OH, n-C_4H_9OH, i-C_4H_9OH, s-C_4H_9OH, and n-$C_5H_{11}OH$ have a relatively large reaction rate constant i.e. $k \geqq 5.6 \times 10^9$ mol^{-1} dm^3 s^{-1}. On the contrary, those which have a chain containing two and less carbon atom such as methanol, ethanol, i-C_3H_7OH and t-C_4H_9OH, exhibit lower reactivity i.e. $k \leqq 3.7 \times 10^9$ mol^{-1} dm^3 s^{-1}. The similar tendency has been observed for the reaction of hydroxy radicals with alcohols in neutral aqueous solutions.[4]

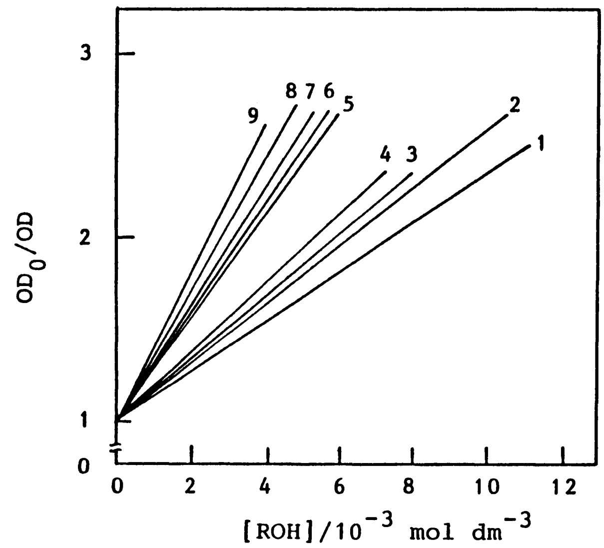

Fig. 2. Determination of rate constants of the reaction of chlorine atoms and alcohols. Plots according to Eq. 4 of the optical density of complexes at 400 nm. (1) CH_3OH, (2) t-C_4H_9OH, (3) C_2H_5OH, (4) i-C_3H_7OH, (5) n-C_3H_7OH, (6) i-C_4H_9OH, (7) s-C_4H_9OH, (8) n-C_4H_9OH, (9) n-$C_5H_{11}OH$.

Table 1. Bimolecular rate constants of the reaction of chlorine atoms with various alcohols

Alcohol	$k/10^9$ mol^{-1} dm^3 s^{-1}
CH_3OH	2.7
C_2H_5OH	3.3
n-C_3H_7OH	5.6
i-C_3H_7OH	3.7
n-C_4H_9OH	7.0
i-C_4H_9OH	5.8
s-C_4H_9OH	6.2
t-C_4H_9OH	3.2
n-$C_5H_{11}OH$	7.9

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