1038 © 1992 The Chemical Society of Japan *Bull. Chem. Soc. Jpn.*, *65*, *1038—1040 (1992)* [Vol. 65, No. 4

Reactivity of the Transient UV-Band Produced in Irradiated Liquid Carbon Tetrachloride with Various Alcohols

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(Received June 26, 1991)

The reactivities of the transient UV-band with a peak at 330 nm produced in irradiated liquid carbon tetrachloride with various alcohols have been measured using the absolute technique of pulse radiolysis. The obtained bimolecular rate constants have been compared with those previously determined for the reaction of chlorine atoms with various alcohols using the competitive scavenging method. The values of reaction rate constants of the UV-band are nearly twice those of chlorine atoms. Similar kinetic isotope effects were observed for deuterated methanol and 2-methyl-2-propanol. However, the dependence on the structure of the alcohols, which is characteristic for hydrogen abstraction from alcohols by chlorine atoms, has not been established by the reaction of the UV-band. These results strongly suggest that the assignment of the UV-band to chlorine atoms is not plausible, and instead, support the assignment to parent cations.

It is well-known that irradiation of liquid carbon tetrachloride at room temperature results in the formation of two distinct optical absorption bands in a UV-vis spectrum region. The spectral data and conflicting assignments are summarized by Emmi et al.[1)] and Washio et al.[2)] The UV-band peaking at 330 nm was first reported by Mehnert et al.[3)] and was assigned to parent cations. Picosecond pulse radiolysis experiments on the formation process of this UV-band have shown the fast formation during 30 ps electron pulse.[4)] On the other hand, Ha et al.[5)] performed the MO calculation of dichlorocarbene and suggested that the UV-band might be dichlorocarbene.

Rather recently, Chateauneuf[6)] measured the reactivity of this UV-band by laser flash photolysis and compared the relative and absolute rate constants with those obtained for the reactions of dichlorocarbene and chlorine atoms. Based on the differences of the relative and absolute values of reaction rate constants, Chateauneuf concluded that the UV-band is not due to dichlorocarbene but to chlorine atoms. In that study our result[7)] of the rate constant of the reaction between chlorine atoms and methanol was cited, however, the agreement was not satisfactory, $(5.7\pm0.3)\times10^9$ $\mathrm{mol^{-1}\,dm^3\,s^{-1}}$ for the UV-band and 2.7×10^9 $\mathrm{mol^{-1}\,dm^3\,s^{-1}}$ for chlorine atoms.

We previously reported that the irradiation of dimethyl sulfoxide in carbon tetrachloride results in the formation of a transient species which exhibits an absorption peaked around 400 nm.[8)] The application of the competition kinetic method using this complex band as a reference system to determine the reactivity of chlorine atoms has been demonstrated.[7)] The rate constants for the reaction of chlorine atoms with various alcohols were reported,[9)] and the validity of the concept of the partial reactivity of specific C–H band was considered.

It should be worth comparing the reactivities of chlorine atoms with a series of alcohols in addition to methanol to examine the Chateauneuf's assignment of the UV-band produced in liquid carbon tetrachloride.

The above considerations have prompted the present work on the reactivity of the UV-band toward various alcohols.

Experimental

Materials. Carbon tetrachloride (Dotite, spectrosol) was used as received. Alcohols were available as high grade commercial products and were used without further purification. Deuterated alcohols were supplied by Aldrich and had the following stated purities in atom %D: CD_3OD (99.5) and $(CD_3)_3OD$ (99+).

Nanosecond Pulse Radiolysis System. The pulse radiolysis apparatus with a time resolution of 10 ns has been described earlier.[10)] Electron pulses of 45 MeV and 10 ns width from an S-band linear accelerator were used as a radiation source. A 1 kW xenon lamp served as the light source. The analyzing light was arranged pararell to the electron beam. The light signals were detected by a photomultiplier (Hamamatsu Photonics R928) and were acquired on a transient digitizer (Iwatsu DM901) combined with an NEC PC-9801 personal computer. The absorbed doses were measured with the KSCN dosimeter.[11)] The dose per pulse was 100—130 Gy. Samples were bubbled with argon in a quartz cell with an optical path length of 1 cm and sealed with a teflon bulb just before irradiation. All experiments were carried out at room temperature (16—18 °C).

Results and Discussion

Reaction Rate Constants of the UV-Band with Alcohols. By pulsing neat carbon tetrachloride with 45 MeV electrons, the UV absorption band with a peak at 330 nm is produced during 10 ns pulse superposing on the underlying absorption and decays by a first order kinetics with a rate constant of $(6.5\pm0.5)\times10^6$ $\mathrm{s^{-1}}$, which is in good agreement with reported half life times, 100 ns.[2,5)] Upon addition of alcohols the decay rate was increased. Typical time profiles of optical absorption are shown in Fig. 1. The pseudo-first-order condition

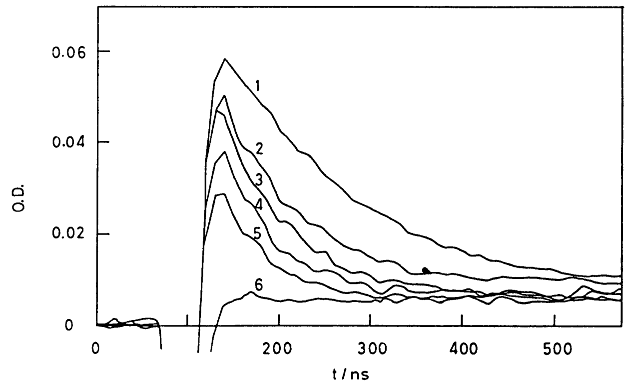

Fig. 1. Effect of the addition of methanol on the kinetic traces of irradiated CCl_4 observed at 335 nm: (1) pure CCl_4; (2) 8.1×10^{-4}; (3) 1.2×10^{-3}; (4) 1.6×10^{-3}; (5) 2.4×10^{-3}; (6) 4.8×10^{-2} mol dm^{-3} methanol in CCl_4.
Dose: 100 Gy.

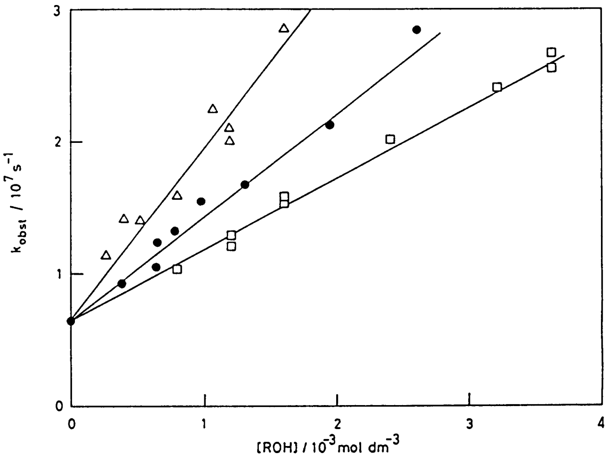

Fig. 2. Concentration dependence of the first order rate constant for reactions of the UV-band produced in CCl_4 with methanol (□), ethanol (●), and 1-hexanol (△).

was employed in this work, i.e., [alcohol]>10^{-4} mol dm^{-3}. Thus the observed pseudo-first-order rate constant, k_{obsd}, can be given by Eq. 1,

$$k_{obsd}=k_0+k[\mathrm{ROH}] \qquad (1)$$

where k_0 and k are the decay rate constant of the transient UV-band in the absence of alcohol and the bimolecular rate constant of the reaction with alcohol, respectively. Figure 2 shows plots of k_{obsd} vs. concentrations of alcohols. As seen from Fig. 2, linear plots were obtained. The rate constants of the reactions of the UV-band with alcohols were calculated from the slope of the straight lines. The rate constants of the UV-band are summarized in Table 1 together with the rate constants of the reaction of chlorine atoms with alcohols which were determined by the competition method using the optical absorption of complexes between chlorine atoms and dimethyl sulfoxide as a reference system.9) The experimental results have been reproduced within ±10%. The value of the rate constant for methanol, 5.4×10^9 mol^{-1} dm^3 s^{-1}, is in good agreement with that reported by Chateauneuf, 5.7×10^9 mol^{-1} dm^3 s^{-1}.6)

For all alcohols under present investigation including deuterated ones, the rate constants are approximately two times greater for the reaction of the UV-band with alcohols than those of the reaction of chlorine atoms with alcohols. The ratio of k(UV-band)/k(Cl) ranges from 1.8 (1-hexanol) to 2.9 (2-methyl-2-propanol).

In Table 2, the UV-band rate constant data for chloroform, dichloromethane, and cyclohexane reported by other researchers are compared with the rate data of chlorine atoms obtained by the competitive method. Although the reported rate constants of the UV-band are rather scattered, they were larger than those of chlorine atoms with an exception of chloroform, as in the case of alcohols.

Table 1. Comparison of the Reaction Rate Constants of the UV-Band and Chlorine Atoms with Alcohols

Alcohol	Reaction rate constant/ 10^9 mol^{-1} dm^3 s^{-1}	
	UV-hand	Cl atoms 9)
Methanol	5.4, 5.7 6)	2.5
Ethanol	7.8	3.1
1-Propanol	8.1	4.2
2-Propanol	9.2	3.5
1-Butanol	9.8	5.1
2-Butanol	8.6	4.2
2-Methyl-1-propanol	8.3	4.3
2-Methyl-2-propanol	8.3	2.9
1-Pentanol	11	5.8
2-Methyl-2-butanol	10	3.9
Cyclopentanol	11	5.3
1-Hexanol	12	6.8
2,3-Dimethyl-2-butanol	12	4.5
Cyclohexanol	14	5.9
Methanol-d_4	3.9	1.5
2-Methyl-2-propanol-d_{10}	3.7	1.6

Table 2. Comparison of the Reaction Rate Constants of the UV-Band and Chlorine Atoms with Chloroform, Dichloromethane, and Cyclohexane

Solute	Reaction rate constant/ 10^9 mol^{-1} dm^3 s^{-1}			
	UV-band			Cl atoms
$CHCl_3$	0.35 3)	0.012 6)	0.03 2)	0.014 12)
CH_2Cl_2	0.1 3)	0.089 6)		0.038 12)
Cyclohexane	10 3)	8.0 6)	7 2)	6.0

Assignment of the 330 nm Band. Agreement between the rate constants determined using absolute technique and the competitive technique is quite unsatisfactory for the alcohols and other compounds investigated. It is worth noting the comparison of the rate

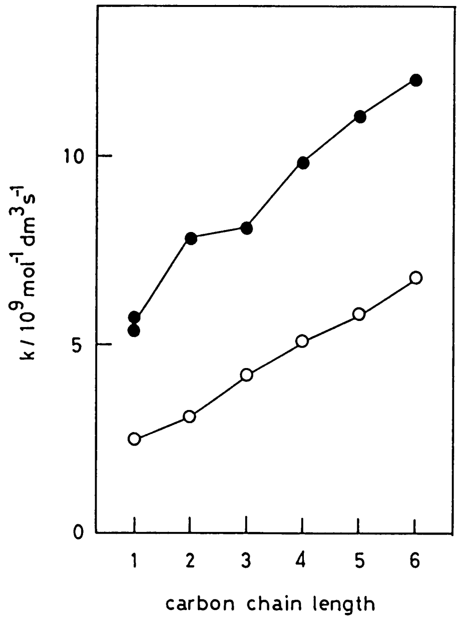

Fig. 3. Effects of alcohol chain length on the reactivity of chlorine atoms (○) and the UV-band produced in CCl_4 (●) toward normal alcohols.

constants of the reaction of the UV-band with a series of normal alcohols with the corresponding rate constants of chlorine atoms. Figure 3 shows a plot of the rate constants of these two transients as a function of the number of carbon atoms in the straight chain alcohols. The parallel increase of the rate constants as seen in Fig. 3 and quite similar kinetic isotope effects observed with deuterated methanol and 2-methyl-2-propanol may indicate a similarity of the reaction mode such as reactive sites both of the UV-band and chlorine atoms with alcohols. However, structual effects of alcohols, which was observed in the case of the reaction of chlorine atoms, was not observed for the UV-band. Among isomers, more branched alcohols, such as 2-methyl-2-propanol, exhibit lower reactivity toward chlorine atoms than the corresponding normal alcohols. The similar tendency has been observed for the reaction of hydroxyl radicals with alcohols in neutral aqueous solutions.13) On the contrary, the results on the reactivity of the UV-band exhibit that the isomeric alcohols have almost the same reaction rate constants. Therefore, the present results demonstrate that the absolute and relative values of the rate constants of the reaction of the UV-band with alcohols are not consistent with those of chlorine atoms.

It can be concluded that the UV-band at 330 nm produced in liquid carbon tetrachloride can be ascribed to parent cations ($CCl_4^{+\bullet}$) as had been assigned by us.4)

The authors are grateful to Dr. Takeaki Enoto and Messrs. Hiroaki Tanida and Koichi Sato for maintaining and operating the LINAC.

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