The Chlorination of Hydrocarbons. XIV.
The Chlorination of Vinyl Compounds[1)]

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The competitive chlorination of various vinyl compounds was carried out in order to elucidate the effect of the structure on the addition rate of chlorine to a double bond. A linear free-energy relationship was found to exist between the reactivities in the presence of oxygen and Taft's σ^* constants. The ρ^* value was calculated to be -1.20. On the other hand, the plot deviated slightly from a straight line; this shows the Taft relationship between the reactivities for the photochlorination and σ^* values, known as an extra acceleration due to the hyperconjugation of the alkyl group.

Paraffin hydrocarbons have been photochlorinated in the liquid phase by Migita and his co-workers.[2,3)] The gas-phase photochlorination of several chloroethanes has also been performed by Mack.[4)] Both groups of workers found Taft's $\rho^*\sigma^*$ relationship to be obeyed. While there have been such extensive studies of the substitutional chlorination, though only a little is known about the addition of chlorine to a double bond.

The effect of the structure on the rate of chlorination was investigated by carrying out competitive reactions with various vinyl compounds.

Experimental

Reagents. All the reagents used in this work were purchased from the Tokyo Kasei Kogyo Co. except for the carbon tetrachloride and hydroquinone, which were obtained from Wako Pure Chemical Industries. They were all of a G.R. or E.P. grade and were not purified further. The chlorine and oxygen were taken from commercial cylinders and were passed through a sulfuric acid trap before use.

Photochemical Procedure. The chlorination was carried out in 100-ml, flat, cylindrical, semibatch Pyrex reactor.[5)] A mixture of two vinyl compounds (both 0.1 mol), hydroquinone (0.001 mol) and hexachloroethane (0.002 mol) in 50 ml of carbon tetrachloride was added to the reactor. Hexachloroethane was useful as the standard material of gas chromatography.

The reactor was immersed in a thermostat at 30 °C and illuminated with a 100-W mercury lamp (Ushio UM-102) placed 5.0 cm above the reaction vessel. The chlorine was fed into the reactor at the rate of 0.1 mol/h. After a period required for the attainment of steady conditions, the irradiation was started. At regular time intervals, 1-ml samples were taken from the reacting solution and analyzed by means of gas chromatography (Shimadzu GC-5, SDC 550 or PEG 6000).

Dark Chlorination Procedure in the Presence of Oxygen. The dark chlorination procedure was the same as that used in the photochemical reaction except for the use of the oxygen. The chlorine and oxygen gases were led from the cylinders through a mixer to the reactor at the rates of 0.1 and 0.04 mol/h respectively.

Results

It is well known that the liquid-phase chlorination of linear olefins gives predominantly addition products, while the chlorination of olefins with branching at the double bond gives predominantly allylic substitution products.[6)] These vinyl compounds were found to give predominantly addition products, accompanied by minor amounts of allylic substitution products. In all the runs, two vinyl compounds were competitively chlorinated in order to keep the effect of the induction period and the concentration of chlorine constant

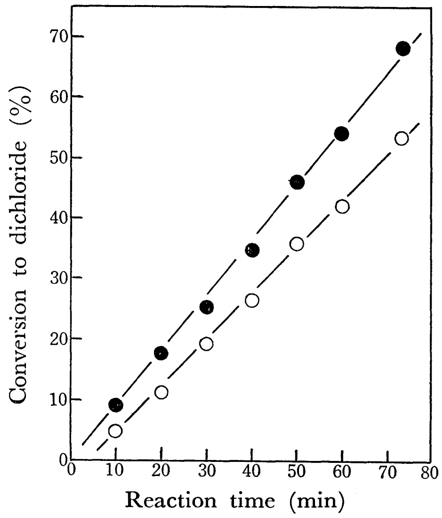


Fig. 1. Competitive photochlorination of allyl chloride and 3-chloro-1-butene at 30 °C.
○: Allyl chloride, ●: 3-chloro-1-butene.

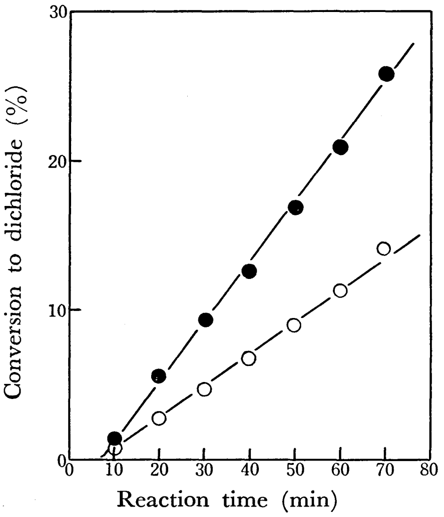


Fig. 2. Competitive chlorination of allyl chloride and 3-chloro-1-butene in the presence of oxygen at 30°C.
○: Allyl chloride, ●: 3-chloro-1-butene.

TABLE 1. RELATIVE RATE CONSTANTS (k/k_0) AND POLAR SUBSTITUENT CONSTANTS (σ^*)

CH$_2$=CH-R	Substituent R	k/k_0		σ^* 8)
		Radical	Ionic	
	$-CN$	0.138	0.00109	3.64a)
	$-COOH$	0.283	0.00197	2.94a)
	$-COOCH_3$	0.383	0.0181	2.00
	$-COCH_3$	—	0.0352	1.65
	$-CH_2CN$	0.601	0.215	1.300
	$-CH_2Cl$	1.00 (standard)	1.00 (standard)	1.050
	$-CH_2Br$	1.57	1.40	1.000
	$-CHClCH_3$	1.17	2.06	0.950a)
	$-CH_2I$	1.73	1.63	0.85
	$-C_6H_5$	1.99	2.00	0.600
	$-CH_2COCH_3$	3.09	—	0.60
	$-CH_2C_6H_5$	1.90	—	0.215
	$-CH_2CH_2CH_2CH_3$	7.01	26.9	−0.130
	$-CH_2CH\genfrac{}{}{0pt}{}{\diagup CH_3}{\diagdown CH_3}$	9.44	35.9	−0.210
	$\diagup CH_3$ $-C-CH_3$ $\diagdown CH_3$	7.72	—	−0.300

a) M. Kosugi, T. Migita, and Y. Nagai, *Nippon Kagaku Zasshi*, **92**, 477 (1971).

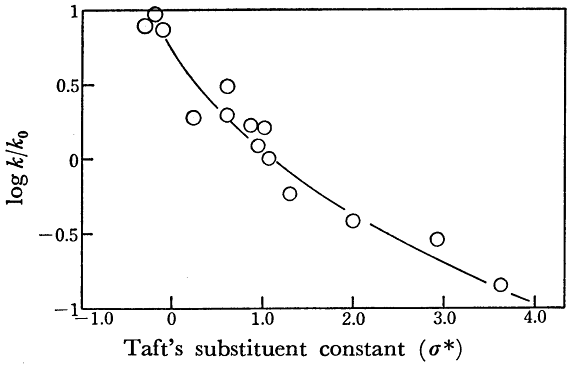


Fig. 3. Taft's plot for photochlorination of vinyl compounds at 30 °C.

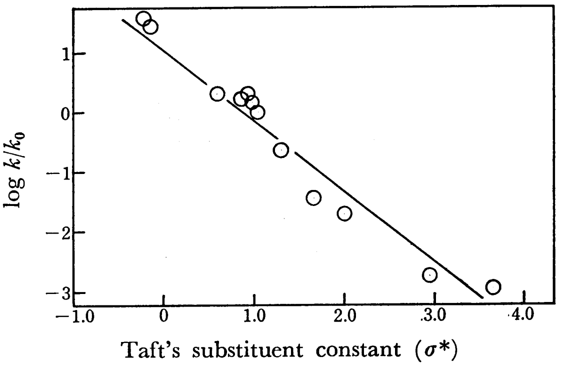


Fig. 4. Taft's plot for chlorination of vinyl compounds in the presence of oxygen at 30 °C.

throughout an experiment. The plots of the conversion of vinyl compounds into the addition products against the reaction time are found to be linear, as is shown in Figs. 1 and 2. Figure 1 shows the competitive photochlorination of allyl chloride and 3-chloro-1-butene as typical experimental data. The results of the competitive chlorination of these compounds for a dark run with oxygen are shown in Fig. 2. The values of the relative rate constants were calculated from the slopes of these straight lines, obtained according to the previous paper.7) These relative rate constants are given in the first two columns of Table 1.

Discussion

As can be seen from Table 1, the rate of chlorination was increased by the electron-releasing substituent group and decreased by the electron-withdrawing group. Since the reactivity seemed to be affected by the polar nature of the substituent, Taft's equation was applied to this chlorination:

$$\log k/k_0 = \rho^*\sigma^*, \tag{1}$$

where k/k_0 is the relative rate constant with respect to the standard reaction (allyl chloride in this case).

The logarithms of the relative rate constants for the photochemical chlorination of vinyl compounds are plotted against Taft's substituent constants, σ^* (Fig. 3). Figure 4 shows also Taft's $\rho^*\sigma^*$ plot for the dark chlorination in the presence of oxygen. It is said that the chlorination of unsaturated compounds in nonpolar media proceeds according to the polar and radical pathways.9) Then, the competitive chlorinations of methyl acrylate and cyclohexane were carried out in order to confirm that either pathway is predominant. The procedure was the same as has been described in the Experimental section. The results of such experiments are summarized in Fig. 5. A dark chlorination under oxygen produced mainly methyl 2,3-dichloropropionate, while chlorocyclohexane was detected in a trace amount. On the other hand, chlorocyclohexane was formed by the substitutive chlorination of cyclohexane for a photochemical reaction. The attack on

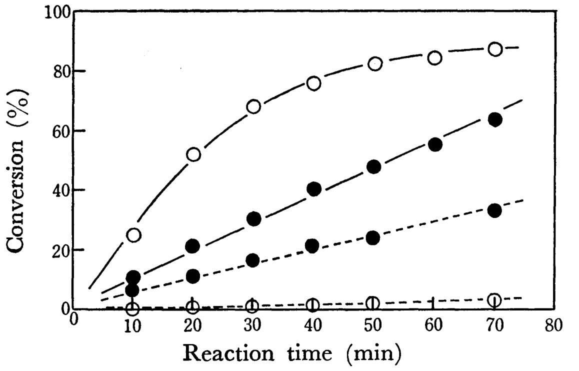


Fig. 5. Competitive chlorination of methyl acrylate and cyclohexane at 30 °C.
○: Chlorocyclohexane from cyclohexane, ●: methyl 2,3-dichloropropionate from methyl acrylate.
——: Illuminated, ----: darkness.

the completely saturated substrate, cyclohexane, is compelling evidence for the presence of free radical chains. The photochlorination took place more rapidly than the dark chlorination in the presence of oxygen, as can be seen by comparing Fig. 1 with 2. This phenomenon is also observed in Fig. 5. In general, the reaction under oxygen became just slow enough to allow a pale yellow color to appear in a solution during the chlorine addition. For a series of dark runs under oxygen, the chlorination of a substrate with an electron-withdrawing group was fairly slow (Table 1).

It has been reported that terminal and linear olefins followed the radical pathway, whereas olefins with carbon-chain branching at the double bond followed the polar pathway.⁹⁾ The polar pathway was also described to be favored by the dilution of the olefin at low olefin concentrations for the dark runs, but this effect could be counteracted with light.¹⁰⁾

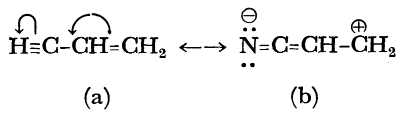
Therefore, it was concluded that the chlorination of these vinyl compounds at higher concentrations under illuminated conditions proceeded predominantly according to the radical pathway. The photochlorination is a radical reaction, while the dark chlorination under oxygen is an ionic one since oxygen acts as a radical inhibitor. The reactivity pattern of the chlorine atom toward vinyl compounds is similar to that of the chlorine molecule, as is shown in Figs. 3 and 4.

A linear free-energy relationship might be found to exist between the relative rate constants of the ionic reaction and Taft's σ^* constants. The ρ^* value was calculated to be -1.20. On the other hand, in the case of the radical reaction, the relative rate constants were slightly more dependent on Taft's σ^* constants than those of the dark runs and the plot seemed to deviate from a straight line, making a concave curve. This phenomenon has been known in connection with the photochlorination of chloroethanes as an extra acceleration by the hyperconjugation effects of the alkyl group.²⁾ Accordingly, it may be thought that the hyperconjugation of the alkyl group is similarly pronounced during the photochlorination of vinyl compounds.

In α-olefin, the electron displacement produced by the electron-releasing alkyl group renders the terminal carbon susceptible to attack by positive chlorine:

$$\mathrm{R{\rightarrow}CH{=}CH_2 \longleftrightarrow R\text{-}\overset{\oplus}{C}H\text{-}\overset{\ominus}{\ddot{C}}H_2.} \qquad (1)$$

On the contrary, nitrile group of acrylonitrile is electron-withdrawing, and the electron displacement causes the unsubstituted carbon atom to become more positive, as is indicated in Formula (a) by a curved arrow.



$$\underset{\text{(a)}}{\mathrm{N{\equiv}C\text{-}CH{=}CH_2}} \longleftrightarrow \underset{\text{(b)}}{\mathrm{\overset{\ominus}{\ddot{N}}{=}C{=}CH\text{-}\overset{\oplus}{C}H_2}} \qquad (2)$$

Owing to the electron displacement, the unsubstituted carbon atom carries a positive charge and is particularly inaccessible to the electrophilic agents (b).

The dark chlorination of vinyl compounds in the presence of the radical inhibitor oxygen proceeds through ionic intermediates. Taft⁶⁾ has suggested that these intermediates can explain an ionic-type mechanism for which the rate-determining step is the addition of a positive chlorine ion to form a carbonium ion and a negative chlorine ion. Therefore, the relative rate constants for the chlorination of various vinyl compounds under oxygen supported an electrophilic attack by the chlorine molecule.

The reactions of chlorine atom with ring-substituted toluenes¹¹,¹²⁾ as well as chloroethanes²,⁴⁾ have been studied, and the chlorine atom might be thought of as an electrophilic radical.

Both reactions are electrophilic and have negative values of ρ^*. The negative values of ρ^* indicate that the electron-donating substituents increase the addition rate of chlorine to the double bond, in agreement with the previous data indicating that the hydrogen abstraction by a chlorine atom is an electrophilic reaction.

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