BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 42 3519—3524 (1969)

Structural Study of the Catalytic Activity of Alkyl Chloride in the Polymerization of *N*-Phenylethylenimine

Tsutomu KAGIYA, Tomizo KONDO and Keigo OBATA
Faculty of Engineering, Kyoto University, Sakyo-ku, Kyoto

(Received May 10, 1969)

The catalytic activity of various alkyl chlorides in the polymerization of *N*-phenylethylenimine was studied from the structural point of view. Both the polymerization rate and the molecular weight of the polymer obtained varied with the kind of alkyl chloride. The rate of monomer consumption is expressed by a first-order rate equation with respect to the monomer concentration in the early stage of the polymerization. The efficiency factors of the catalysts differ with the kind of alkyl chloride and increase with an increase in the reaction time. When the chloride of a conjugated alkyl group is used, the polymerization rate decreases with an increase in the ionization potential of the alkyl radical, while it increases when chlorides of a non-conjugated alkyl are used. The structural study of the catalytic activity of the alkyl chloride was made quantitatively from the energetic point of view.

It has already been reported by the present authors[1] that, in the polymerization of *N*-phenylethylenimine withv arious carboxylic acid catalysts ($pK_a=0.23$—4.87), there was no chain transfer reaction, and that the rates of the initiation, propagation, and termination reactions increased with a decrease in the pK_a values of the acids. These results indicate that the rates of the elementary reactions are dependent on the structural nature of the catalyst.

The purpose of this paper is to investigate the relation between the polymerization rate and the structure of the alkyl chloride catalyst in the polymerization of *N*-phenylethylenimine.

Experimental

The methods of preparing and purifying *N*-phenylethylenimine were described in the previous paper.[1] Acetonitrile and alkyl chlorides of a guaranteed reagent were purified by the usual method.[2]

The methods of the polymerization of the polymer and the determination of its molecular weight were also described in the previous paper.[1] The polymerization was carried out under the following conditions: monomer, 0.01 mol; acetonitrile as the solvent, 5 m*l*; catalyst, 0.00067 mol; temperature, 0°C.

The infrared spectrum of the polymer was measured by the use of the potassium bromide pellet technique on a Shimadzu infrared spectrophotometer, Model IR-27.

Results and Discussion

The Infrared Spectrum of the Polymer. The infrared spectrum of the polymer initiated with allyl chloride shows the characteristic peaks at 910 cm^{-1} and 930 cm^{-1} assigned to the vinyl group and the piperazine ring respectively. This may indicate that the polymer contains the allyl group and the piperazine ring at both ends of the polymer. Therefore, it may be considered that this polymerization is initiated with alkyl chloride and is terminated by forming the piperazine ring at the end of the polymer, as has been described in the previous paper.[1]

Polymerization with Various Alkyl Chlorides. The plots of the polymer yield ($[M_p]$; polymerized monomer mol/*l*) against the reaction time are shown in Figs. 1 and 2. The curves of these figures show that the polymerization rate varies markedly with the kind of alkyl chloride. As is shown in Fig. 3, the rate of the monomer consumption is expressed by a first-order rate equation with respect to the monomer concentration in the early stage of the polymerization (polymer yield $<20\%$). In view of this fact, it is considered that the steady-state assumption that the initiation rate is equal to the termination one is applicable in the early stage of this polymerization.

The relations between the number-average molecular weight ($\overline{M}_n$) and the reaction time are shown in Fig. 4. The molecular weight is almost constant regardless of the reaction time. This may be ascribed, not to the chain transfer, but to the fact that the steady-state assumption is applicable, for, as has been described in the previous paper,[1]

---

[1] T. Kagiya, T. Kondo and K. Fukui, This Bulletin, **41**, 2473 (1968).

[2] A. Weissberger, E. S. Proskauer, J. A. Riddick and E. E. Toops, "Technique of Organic Chemistry, Vol VII, Organic Solvents," Interscience Publishers, Inc., New York (1955).

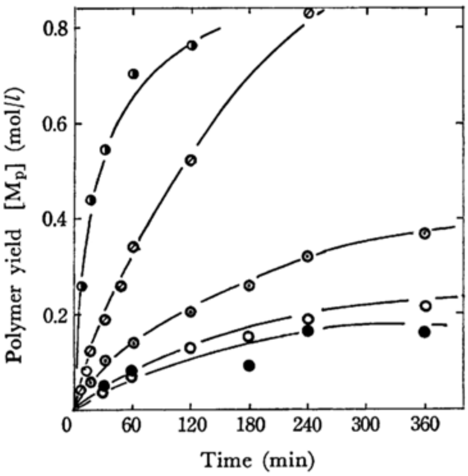


Fig. 1. Polymer yield ([M$_p$]) *vs.* polymerization time.
◑, Triphenylmethyl; ⊘, Phenyl; ⊙, Benzyl; ○, *β*-Methallyl; ●, Allyl

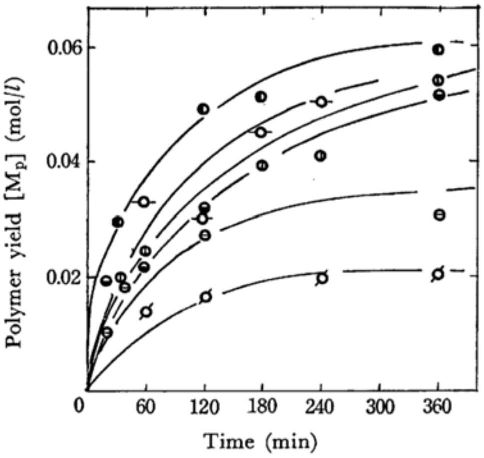


Fig. 2. Polymer yield ([M$_p$]) *vs.* polymerization time.
◐, *n*-Butyl, -○-, Phenyl; ⦶, Isobutyl; ◑, Isopropyl; ⊖, Ethyl; ⌀, *t*-Butyl

there is essentially no chain transfer in the polymerization of *N*-phenylethylenimine. On the other hand, since the structure of the initiating and propagating species depend on only the chlorine atom of the chlorides, the rate constant of the propagation and termination reactions may be considered to be constant regardless of the kind of chloride. Therefore, the difference in the molecular weight with the kind of chloride may be due to the difference in the initiation rate constant. These fact will be discussed below.

In the polymerization without chain transfer and bimolecular termination, the value of $[M_p]/([C]_0\overline{M}_n)$ is called the efficiency factor of the catalyst (α), where, $[C]_0$ is the initial catalyst concentration. The increase in α with an increase in the reaction time (Fig. 5) indicates that the initiation reaction occurs continuously during the course of the polymerization. Moreover, since α differs greatly from alkyl chloride to alkyl chloride (about from 1×10^{-4} to 0.8), there is perhaps a very large difference in the initiation rate as well. From these facts, it is assumed that the difference in the polymerization rate with the kind of alkyl chlorides is due to the difference in the rate constant of the initiation reaction.

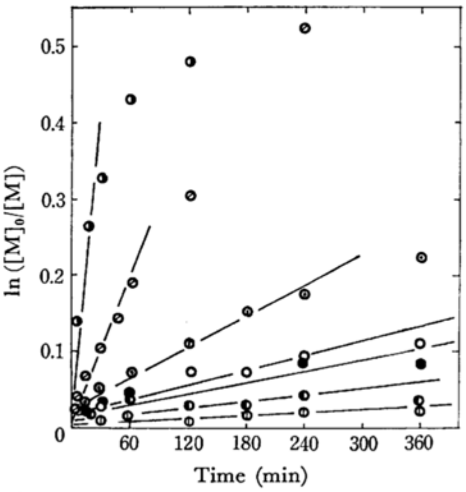


Fig. 3. Plots of $\ln([M]_0/[M])$ against reaction time.
The notes are the same as Fig. 1 and Fig. 2.

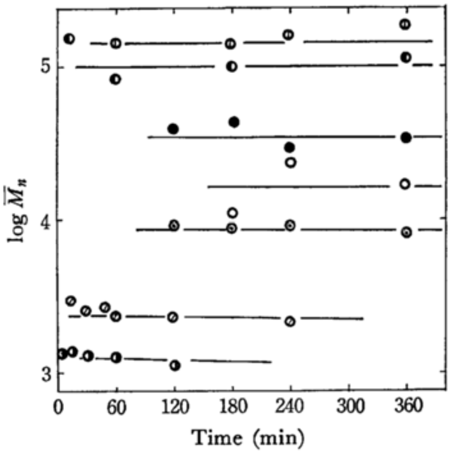


Fig. 4. Relation between the molecular weight ($\overline{M}_n$) of the polymer and reaction time.
The notes are the same as Fig. 1 and Fig. 2.

Since the initiation reaction may be the addition reaction of alkyl chloride with *N*-phenylethylenimine, the initiation reaction is expected to proceed by the same mechanism as the Menschutkin reaction, as will be described later in connection with Eq. (1). Therefore, the polymerization rates (k), defined as the slopes of the straight lines in Fig. 3,

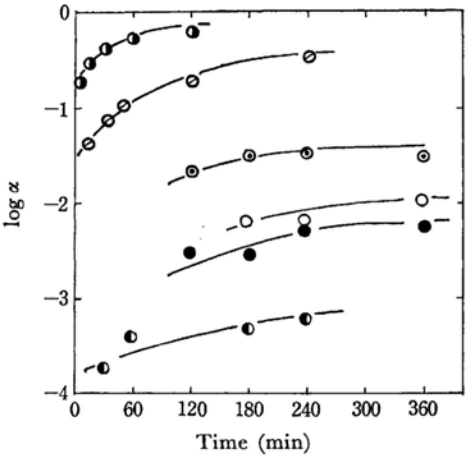


Fig. 5. Plots of log α against reaction time. The notes are the same as Fig. 1 and Fig. 2.

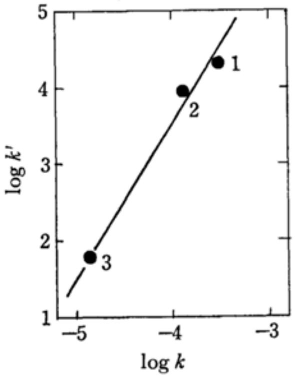


Fig. 6. Relation between the rate constant (k') of Menschutkin reaction (RI+Di-Me-Aniline) and polymerization rate (k) with the use of RCl.
R: 1, Benzyl; 2; Allyl; 3, Ethyl

were studied in comparison with the rate constant of the Menschutkin reaction. The plots of the k values against the rate constants in the reaction of alkyl iodides with dimethylaniline,[3] which had a structure similar to that of *N*-phenylethylenimine, are shown in Fig. 6. The fact that the rate of the Menschutkin reaction is almost proportional to the polymerization rate is in good accordance with the above assumption.

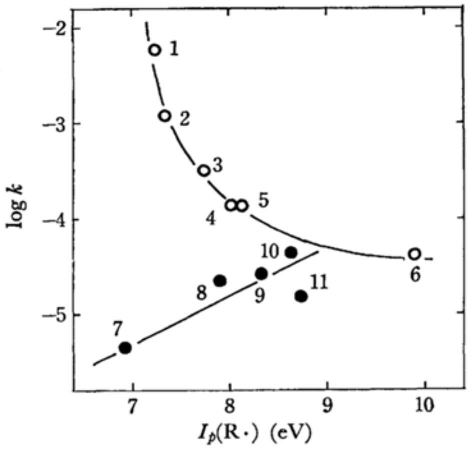


Fig. 7. Relation between the polymerization rate (k) and $I_p(R)$ of alkyl chloride.
Conjugated alkyl: 1, Triphenylmethyl; 2, Phenyl; 3, Benzyl; 4, β-Methallyl; 5, Allyl; 6, Phenyl.
Non-conjugated alkyl: 7, *t*-Butyl; 8, Isopropyl; 9, Isobutyl; 10, *n*-Butyl; 11; Ethyl

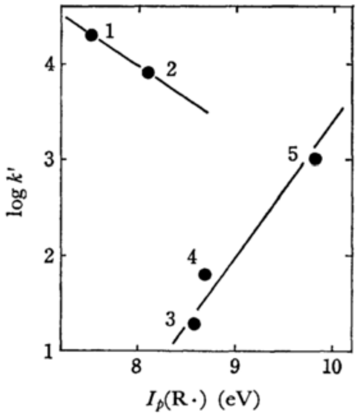


Fig. 8. Relation between the rate constant (k') and $I_p(\mathrm{R}\cdot)$ in Menschutkin reaction (RI + Di-Me-Aniline).
1, Benzyl; 2, Allyl; 3, *n*-Propyl; 4, Ethyl; 5, Methyl

Since the peculiar nature of alkyl chloride (RCl) is considered to be caused by the difference in the electronic nature of the alkyl radical, the k value was plotted against the ionization potential of the alkyl radical ($I_p(\mathrm{R}\cdot)$) (Fig. 7). There is a good relation between the catalytic activity and the ionization potential of the alkyl radical; the curves may be classified into two groups, that is, alkyl chloride with the conjugated alkyl group and that with the non-conjugated alkyl one. With the catalysts of the chloride of the conjugated alkyl group, the polymerization rate decreases with an increase in the $I_p(\mathrm{R}\cdot)$ value, while it increases in the non-conjugated alkyl group.

On the other hand, it is found that the relation between the rate constant of the Menschutkin reaction and the $I_p(\mathrm{R}\cdot)$ value of the alkyl chloride is similar to the relation in this polymerization, as Fig. 8 shows. The structural study of these reactions will be discussed below.

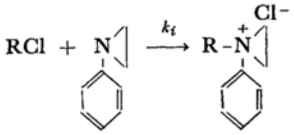
Kinetics. From these experimental facts and the results obtained in the previous paper,[1] the

---

[3] R. W. Prestone and H. D. Jones, *J. Chem. Soc.*, **101**, 1930 (1912).

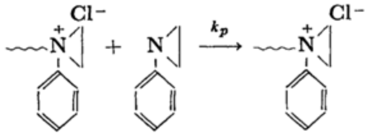
following mechanism of the polymerization may be postulated:

Initiation:



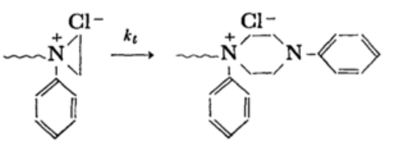
(I) (1)

Propagation:



(2)

Termination:



(3)

The initiating step may be the reaction of the alkyl chloride with *N*-phenylethylenimine to produce the initiating species, compound (I). As has been mentioned in the previous paper,[1)] the polymer chain is considered to terminate with the formation of the piperazine derivative ring.

According to the mechanism of the polymerization postulated, the rate equations of the elementary reactions may be written as follows:

$$R_i = k_i[\mathrm{RCl}][\mathrm{M}] \tag{4}$$

$$R_p = k_p[\mathrm{P^*}][\mathrm{M}] \tag{5}$$

$$R_t = k_t[\mathrm{P^*}][\mathrm{M}] \tag{6}$$

where,

[RCl], [M], [P*]; the concentrations of the catalyst, the monomer, and the propagating species;

R_i, R_p, R_t: the rates of the initiation, propagation, and termination reactions, and

k_i, k_p, k_t: the rate constants of the initiation, propagation, and termination reactions.

Considering that the concentration of the monomer is much larger than that of the catalyst, Eq. (4) may be expressed by Eq. (7):

$$R_i = k_i[\mathrm{RCl}] \tag{7}$$

Since, in the early stage of the polymerization, the steady-state is realized ($R_i = R_t$), Eq. (8) is obtained:

$$k_i[\mathrm{RCl}] = k_t[\mathrm{P^*}] \tag{8}$$

On the other hand, from Eq. (7) the concentration of the catalyst can be expressed by Eq. (9):

$$[\mathrm{RCl}] = [\mathrm{RCl}]_0 e^{-k_i t} \tag{9}$$

Then, from Eqs. (8) and (9), the concentration of the propagating species can be represented by Eq. (10):

$$[\mathrm{P^*}] = (k_i/k_t)[\mathrm{RCl}]_0 e^{-k_i t} \tag{10}$$

By substituting [P*] into Eq. (5) and by then integrating it, Eq. (11) is derived:

$$\ln([\mathrm{M}]_0/[\mathrm{M}]) = (k_p/k_t)[\mathrm{C}]_0\,(1-e^{-k_i t}) \tag{11}$$

In the early stage of the polymerization, Eq. (11) may be represented approximately by Eq. (12):

$$\ln([\mathrm{M}]_0/[\mathrm{M}]) = (k_i k_p/k_t)[\mathrm{RCl}]_0 t \tag{12}$$

The fact that the molecular weight is almost constant, regardless of the reaction time, and the fact that it differs with the kind of alkyl chloride may be explained as follows. If there is no chain-transfer reaction, the number average of the degree of the polymerization, $\overline{P_n}$, is represented by Eq. (13):

$$\overline{P_\mathrm{n}} = \int R_p \mathrm{d}t \Big/ \int R_i \mathrm{d}t \tag{13}$$

The polymer yield, $[\mathrm{M_p}]$, is expressed by Eq. (14):

$$[\mathrm{M_p}] = [\mathrm{M}]_0 - [\mathrm{M}] \tag{14}$$

Therefore, from Eqs. (11) and (14), Eq. (15) is derived:

$$[\mathrm{M_p}] = [\mathrm{M}]_0 \left\{1 - \exp \frac{k_p}{k_t}[\mathrm{C}]_0(1-e^{-k_i t})\right\} \tag{15}$$

On the other hand, $\int R_i \mathrm{d}t$ is expressed by Eq. (16):

$$\int R_i \mathrm{d}_t = [\mathrm{C}]_0 - [\mathrm{C}] = [\mathrm{C}]_0(1-e^{-k_i t}) \tag{16}$$

Therefore, by combining Eqs. (13), (15), and (16), $\overline{P_n}$ may be written by Eq. (17):

$$\overline{P_n} = \frac{[\mathrm{M}]_0\left\{1 - \exp \frac{k_p}{k_t}[\mathrm{C}]_0(1-e^{-k_i t})\right\}}{[\mathrm{C}]_0(1-e^{-k_i t})} \tag{17}$$

Figure 9 shows the plots of $\overline{P_n}$ against the reaction time assuming that $(k_p/k_t)[\mathrm{C}]_0 = 10$ in Eq. (17). From Fig. 9 it may be seen that the variation in $\overline{P_n}$ is small within the definite period of the reaction time, and that the value of $\overline{P_n}$ differs with the value of k_i. These facts are considered to agree with the results shown in Fig. 4.[*1]

Energetic Study of the Initiation Reaction. The relation between the kind of alkyl chloride and the initiation rate was studied quantitatively from the energetic point of view. The initiation reaction may be written by Eq. (18) in view of the

---

[*1] In the case of the polymerization of *N*-phenylethylenimine with various carboxylic acids (pK_a=2.85—4.87), the molecular weight of the polymer was almost constant in the early stage of the polymerization, whereas in the later stage of the polymerization it increased. This may indicate that, in the early stage of the polymerization, the steady-state method is applicable, but not in the later stage. Although the steady-state method is thus not applicable in all periods of the reaction time, in order to estimate the rate constant of the initiation reaction the steady-state method was used.

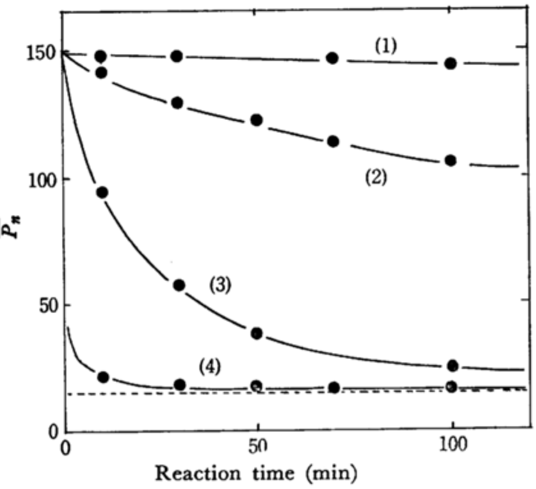
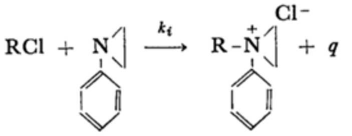


Fig. 9. The plots of $\overline{P}_n$ against the reaction time assuming $(k_p/k_t)\ [C]_0=10$ in Eq. (17).
The value of k_i: (1) 0.0001, (2) 0.001, (3) 0.01, (4) 0.1

heat of reaction (q);



(18)

If it can be assumed that the relation between the activation energy and the heat of reaction is:

$$\Delta E = C_1 - C_2 q \tag{19}$$

the initiation rate can be evaluated by the heat of reaction as follows:

The heat of the reaction of the initiation reaction is considered to depend on the energy needed for dissociation of alkyl chloride to give the alkyl cation and the chlorine anion and for the addition of the alkyl cation to *N*-phenylethylenimine. The ionic dissociation energy of the alkyl chloride is considered to be proportional to the value of $-D(\mathrm{RCl})-I_p(\mathrm{R}\cdot)+E_a(\mathrm{Cl}\cdot)+\mathrm{T}\Delta\mathrm{S}$, with the same solvent system, where $D(\mathrm{RCl})$, $I_p(\mathrm{R}\cdot)$, $E_a(\mathrm{Cl}\cdot)$, and $\mathrm{T}\Delta\mathrm{S}$ are the bond dissociation energy of the alkyl chloride, the ionization potential of the alkyl radical, the electron affinity of the chlorine, and the entropy term respectively. Since the addition of the alkyl cation to *N*-phenylethylenimine may be the electrophilic reaction of the alkyl cation to *N*-phenylethylenimine and the nucleophilic reaction of *N*-phenylethylenimine to the alkyl cation, it may be considered that the larger the electron affinity of the alkyl cation ($E_a(\mathrm{R}^+)=I_p(\mathrm{R}\cdot)$) and the ionization potential of *N*-phenylethylenimine (I_p(Imine)), the smaller the energy of the addition of the alkyl cation to *N*-phenylethylenimine. On the basis of these considerations, the following empirical expression can be proposed for the evaluation of the heat of reaction of the initiation reaction in Eq. (18):

$$q = -D(\mathrm{RCl}) - I_p(R\cdot) + E_a(\mathrm{Cl}\cdot) + T\Delta S + C_3 I_p(\mathrm{R}\cdot) - C_4 \mathrm{I}_p(\mathrm{Imine}) + C_5 \tag{20}$$

Considering that $E_a(\mathrm{Cl}\cdot)$ and I_p(Imine) are constant and that, in the experiment with the same solvent, the value of TΔS is almost constant, Eq. (20) may be written in the form:

$$q = -D(\mathrm{RCl}) - I_p(\mathrm{R}\cdot)(1 - C_3) + C_6 \tag{21}$$

By a combination of Eqs. (19) and (21), the activation energy may be expressed by Eq. (22):

$$\Delta E = C_1 - C_2\{-D(\mathrm{RCl}) - I_p(\mathrm{R}\cdot)(1 - \mathrm{C}_3) + C_6\} \tag{22}$$

Subsequently, we tried to express the bond-dissociation energies of alkyl halides as a function of $I_p(\mathrm{R}\cdot)$ and $E_a(\mathrm{R}\cdot)$. As is shown in Fig. 10, the dissociation energy of alkyl halide increases almost in proportion to the value of $I_p(\mathrm{R}\cdot)-E_a(\mathrm{R}\cdot)$.

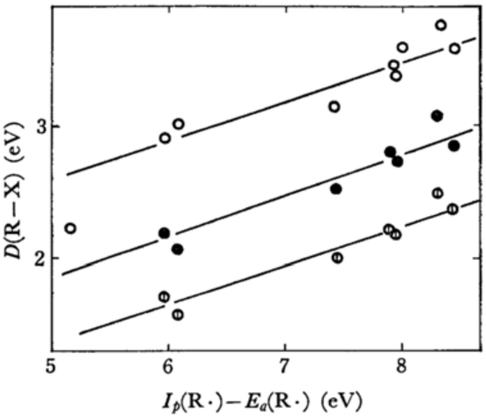


Fig. 10. Relation between the dissociation energy of alkyl halide and the value of $I_p(\mathrm{R}\cdot)-E_a(\mathrm{R}\cdot)$ of alkyl radical.
○, Chloride; ●, Bromide; ⦶, Iodide

The empirical equation (23) was, then, obtained for the dissociation energy of alkyl chloride:

$$D(\mathrm{RCl}) = 0.3\{I_p(\mathrm{R}\cdot) - E_a(\mathrm{R}\cdot)\} + 1.1 \tag{23}$$

By substituting Eq. (23) into Eq. (22), the activation energy may be expressed in terms of $I_p(\mathrm{R}\cdot)$ and $E_a(\mathrm{R}\cdot)$:

$$\Delta E = C_7 + C_2(1.3 - C_3)I_p(\mathrm{R}\cdot) - 0.3E_a(\mathrm{R}\cdot) \tag{24}$$

On the other hand, from the plots of $E_a(\mathrm{R}\cdot)$ against $I_p(\mathrm{R}\cdot)$, as is shown in Fig. 11, $E_a(\mathrm{R}\cdot)$ is found to be approximately given by the following relations in the range of $7.8 \leq I_p(\mathrm{R}\cdot) \leq 9.9$: for the conjugated alkyl radical:

$$E_a(\mathrm{R}\cdot) \fallingdotseq 2.0 \tag{25}$$

and for the non-conjugated alkyl radical:

$$E_a(\mathrm{R}\cdot) \fallingdotseq 0.45\, I_p(\mathrm{R}\cdot) - 3.0 \tag{26}$$

Hence, the activation energy may be written in these forms:

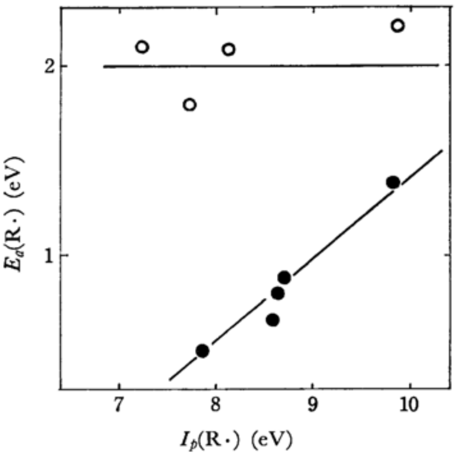


Fig. 11. Relation between electron affinity E_a(R·) and ionization potential I_p(R·) of alkyl radical.
○, conjugated alkyl radical
●, non-conjugated alkyl radical

for the conjugated alkyl radical:

$$\Delta E = (C_7 - 0.6) + C_2(1.3 - C_3)I_p(\mathrm{R}\cdot) \tag{27}$$

and for the non-conjugated alkyl radical:

$$\Delta E = (C_7 + 0.9) + C_2(1.17 - C_3)I_p(\mathrm{R}\cdot) \tag{28}$$

On the other hand, the rate constant is expressed by Eq. (29):

$$\ln k_i = \ln A - \Delta E/\boldsymbol{RT} \tag{29}$$

By substituting Eq. (27) or (28) into Eq. (29), Eqs. (30) and (31) were obtained for the conjugated alkyl radical:

$$\ln k_i = (0.6/\boldsymbol{RT} + C_8) + (C_2/\boldsymbol{RT})(1.3 - C_3)I_p(\mathrm{R}\cdot) \tag{30}$$

and for the non-conjugated alkyl radical:

$$\ln k_i = (-0.9/\boldsymbol{RT} + C_8) + (C_2/\boldsymbol{RT})(1.17 - C_3)I_p(\mathrm{R}\cdot) \tag{31}$$

If $1.17 < C_3 < 1.30$ and $C_2 > 0$, then:
for the conjugated alkyl radical:

$$1.3 - C_3 < 0 \tag{32}$$

and for the non-conjugated alkyl radical:

$$1.17 - C_3 > 0 \tag{33}$$

Therefore, if the values of C_3 and C_2 satisfy the above assumption, these considerations can explain the experimental results with the catalysts of conjugated and non-conjugated alkyl chlorides shown in Fig. 7.