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RADIATION-INDUCED CYCLOREVERSION OF INDENE CYCLOBUTANE DIMERS IN n-BUTYL CHLORIDE BY A CHAIN REACTION MECHANISM

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The cycloreversion of _trans,syn_- and _cis,syn_-indene dimers (I and II) occurred upon γ-radiation of n-butyl chloride solutions. The effects of additives and high G values for formation of indene demonstrated that the cycloreversion proceeds by means of a chain reaction mechanism involving cation radicals as chain carriers.

Ion radicals are important intermediates in radiation chemistry and can be selectively formed by radiolyses of organic solutions.[1)] However, radiolytic chain reactions which involve ionic species as chain carriers have been scarcely published except polymerization reactions; radiation-induced chain isomerizations of _cis_-2-butene and _cis_-stilbene occur _via_ the cation radical and the anion radical respectively.[2,3)] We have found that chain cycloreversion of I and II occurs upon γ-radiation of n-butyl chloride solutions, while the other similar compounds, III IV, and V are stable to the γ-radiolysis.

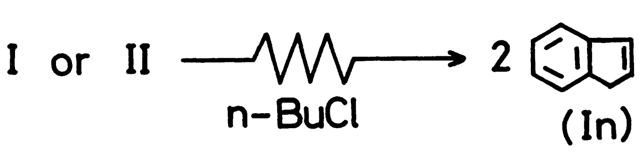

I


II


III

IV

V



Solutions of I in n-butyl chloride were degassed by freeze-pump-thaw cycles under a high vacuum and irradiated with 4 KCi ^{60}Co at room temperature. GLC showed that indene is the only detectable product and that the formation increased linearly with irradiation time up to ca. 20% conversion. This reaction was completely quenched by 0.1 M of either methanol or 1,4-dimethoxybenzene, but not at all by molecuar oxygen (Table 1 and Fig. 2). The effects of additives prove that the cycloreversion proceeds by means of a cation radical mechanism and that neither excited species nor free radicals participate in the reaction at all. In Fig. 1 is shown a linear plot of G(In)$^{-1}$ vs. [I]$^{-1}$, from which the limiting G value (G$^{\infty}$) was determined to be 67.

Table 1. Effects of additives and dose rate in γ-radiolysis of I in n-butyl chloride[a)]

	Additives[b)]					Dose rate (×10^{-19} eV/g·h)		
	None	O_2[c)]	CH_3OH	Indene		6.19	1.29	0.976
			(0.1 M)	(10^{-3} M)	(5×10^{-3} M)			
G(In)	40.0	39.6	<0.1	18.8	10.6	42.8	40.9	37.9

a) [I] = 10^{-2} M. b) Dose rate; 1.29×10^{19} eV/g·h. c) Air-saturated.

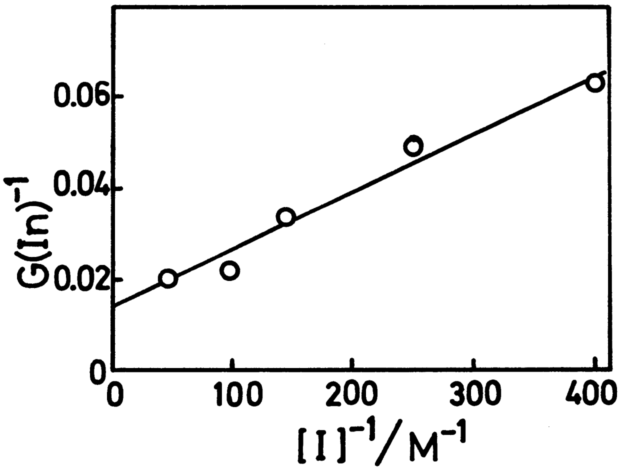


Fig. 1. Plot of G(In)$^{-1}$ vs. [I]$^{-1}$; dose rate, 1.29×10^{19} eV/g·h.

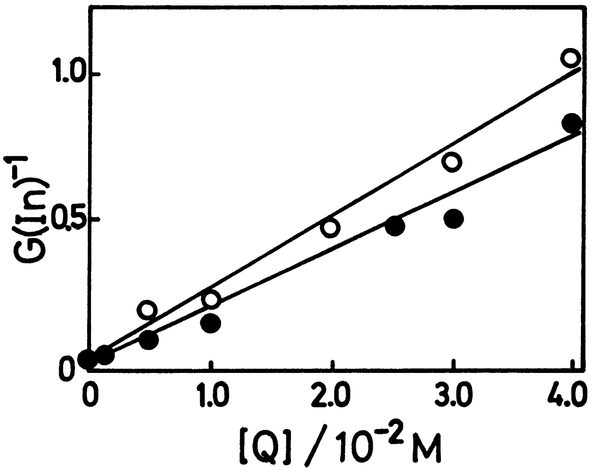


Fig. 2. Stern-Volmer plots for quenching by 1,4-dimethoxybenzene (-○-) and 1,1-dimethylindene (-●-); [I] = 10^{-2} M; dose rate, 1.29×10^{19} eV/g·h.

γ-Radiation of n-butyl chloride solution is known to give n-butyl chloride cation ($BuCl^{\dagger}$)[1,4] in the G value of *ca.* 3,[1] which decays within 80 μs at 113 K to give butene cations.[4] Therefore, G^{∞} clearly demonstrates the occurrence of a chain reaction. As has been discussed in the redox-photosensitized cycloreversion of I,[5] it is suggested that the cycloreversion of I is catalyzed by cation radicals without hole transfer. For mechanistic elucidation, therefore, we propose the following mechanistic pathways, where $S^{\dagger}$ and Q represent the chain carrier and 1,4-dimethoxybenzene respectively.

$$\begin{array}{lll}
BuCl & \rightsquigarrow & BuCl^{\dagger} + e^{-} \quad (G_0 \simeq 3) \\
BuCl + e^{-} & \longrightarrow & Bu\cdot + Cl^{-} \\
BuCl^{\dagger} & \xrightarrow{k_d} & C_4H_8^{\dagger} \ (\text{+ Other products}) \\
S^{\dagger} + (I) & \xrightarrow{k_r} & S^{\dagger} + 2(In) \\
S^{\dagger} + (I) & \xrightarrow{k_{ht}} & S + (I)^{\dagger} \\
S^{\dagger} + Q & \xrightarrow{k_q} & S + Q^{\dagger} \\
(I)^{\dagger} & \xrightarrow{k_c} & (In)^{\dagger} + (In) \\
(In)^{\dagger} & \longrightarrow & \text{Other product(s)}
\end{array}$$

As the chain carrier, indene cation, $(In)^{\dagger}$, can be safely discarded, since the cycloreversion was quenched by either 1,1-dimethylindene or indene. For $(I)^{\dagger}$ to act as the chain carrier, the lifetime should be longer than 100 ns,[6] being unusually long compared with that of tetraphenylcyclobutane cation; it is estimated to be much shorter than 10 ns.[7] Therefore, $(I)^{\dagger}$ appears to be unfavorable for the chain carrier. If $BuCl^{\dagger}$ is the chain carrier, Eq. 1 can be derived, being in accord with the linear relationships of $G(In)^{-1}$ *vs.* $[I]^{-1}$ and [Q] in Figs. 1 and 2.

$$\frac{1}{G} = \frac{1}{G_0}\left(\frac{k_{ht}}{2k_r + k_{ht}}\right)\left(1 + \frac{k_d + k_q[Q]}{k_{ht}[I]}\right) \quad \cdots\cdots\cdot \ (1)$$

Provided $k_q \simeq 10^{10}\ M^{-1}s^{-1}$ and $G_0 \simeq 3$, the following rate constants are obtained; $k_r \simeq 10^{10}\ M^{-1}s^{-1}$, $k_{ht} \simeq 10^{9}\ M^{-1}s^{-1}$, and $k_d \simeq 8\times10^{6}\ s^{-1}$. The value of k_r suggests that the catalytic cleavage occurs on every collision. However, detailed discussion requires further investigation. For example, $S^{\dagger}$ may be a "vibrationally excited" hole[4] or a relaxed hole; hole capture by Q or by I may occur by a hole migration process or by a charge transfer process.

The radiolytic cycloreversion of II was more efficient than that of I; the value at 10^{-2} M of II was 56.7. This can be reasonably understood, since II is more strained owing to the cis-configuration than I. In contrast, III, IV, and V were not radiolytically cleaved in n-butyl chloride. The occurrence of radiolytic cycloreversion of cyclobutane compounds in n-butyl chloride would thus depend on stereoelectronic structures of compounds. For example, a through-bond interaction between two π-electron systems can occur in I and II but not in III. In this regard, it should be noted that the oxidation potential of I (1.32 V)8) is identical to that of II but significantly lower than that of III (1.49 V). Moreover, ring strain energies should be also taken into consideration; the inertness of IV and V to the catalytic cycloreversion would arise mainly from the less strained structure. Details are now under extensive investigation.

References and Notes

1) W. H. Hamill, in "Radical Ions," ed by E. T. Kaiser and L. Kevan, John Wiley & Sons, New York, N. Y. (1968), p. 321.

2) Y. Harata, M. Matsui, and M. Imamura, Chem. Lett., 199 (1977).

3) R. R. Hentz, K. Shima, and M. Burton, J. Phys. Chem., 71, 461 (1967).

4) S. Arai, A. Kira, and M. Imamura, J. Phys. Chem., 80, 1968 (1976).

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6) If $(\mathrm{I})^{\overset{+}{\cdot}}$ is the chain carrier, the rate equation does not agree with the results in Figs. 1 and 2. However, Eq. 2 can be obtained by taking into account of the process, $(\mathrm{I})^{\overset{+}{\cdot}} + (\mathrm{I}) \xrightarrow{k_t} (\mathrm{In})^{\overset{+}{\cdot}} + 3(\mathrm{In})$, and assuming that $k_{ht}[\mathrm{I}] \gg k_d$ and $2k_r[\mathrm{I}] \gg k_c$. If $k_r \simeq 10^{10}\ \mathrm{M}^{-1}\mathrm{s}^{-1}$, k_c is $8.5\times10^{6}\ \mathrm{s}^{-1}$; this is the maximum value.

$$\frac{1}{G} = \frac{1}{G_0}\left(\frac{k_t}{2k_r + 3k_t}\right)\left(1 + \frac{k_c + k_q[\mathrm{Q}]}{k_t[\mathrm{I}]}\right) \quad \cdots\cdots\cdots \quad (2)$$

7) S. Takamuku, S. Miki, and H. Sakurai, unpublised results.

8) Measured by cyclic voltammetry in acetonitrile vs. Ag/Ag^{+}, using $\mathrm{Et_4NBF_4}$ as supporting electrolyte.

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