The Efficiency of the Internal Conversion Process in Br80

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SEVERAL values for the efficiency of internal conversion of Br^{80} (4.5 hr.) have been reported. Previous studies of chemical effects accompanying this nuclear reaction carried out in condensed phases have given values of 0.85 to 0.90.[1] According to recent physical measurements,[2] the transition proceeds in two steps, one of which is apparently completely internally converted, as evidenced by failure to find the corresponding unconverted gamma-ray. This should lead to chemical activation in every decay, although the ultimate chemical effect will depend upon the environment.

Since we plan to undertake quantitative kinetic studies with Br^{80} (4.5 hr.) in gaseous systems, it is first necessary to measure the conversion efficiency in terms of the chemical effects produced in a gaseous system, and to correlate quantitatively, if possible, chemically and physically measured conversion efficiencies. To achieve maximum separation of parent and daughter activities it is probably necessary to avoid the cage effect of the liquid phase, to introduce the parent into a relatively stable molecular form, and to add an acceptor which will readily combine or exchange with the nascent daughter particles. Finally it must be possible to remove Br^{80} (18 min.) and begin counting Br^{80} (4.5 hr.) within a brief interval since the ratio of the counting rates at zero time (moment of separation) is a measure of conversion efficiency. The following procedure proved to be satisfactory. The total bromine activity, as AgBr*, was converted to AlBr$_3$* and exchanged with CH$_3$Br*; water was added to destroy AlBr$_3$ and CH$_3$Br* was then distilled from P$_2$O$_5$ and HBr (0–50-mole percent) was added. This gaseous mixture remained at room temperature for two hours. The CH$_3$Br* was transferred to the cold finger of a gas sample holder surrounding a thin-wall counter within an interval of ten seconds: HBr was removed during the transfer by an interposed soda-lime tube. Counting of the gas sample, at a fraction of its vapor pressure, started within thirty seconds and continued through the decay of Br^{82}. In our counting arrangement the counting efficiency of Br^{80} (4.5 hr.) is quite negligible and therefore its activity must be measured through its 18-min. daughter. After correcting for a small Br^{82} (34 hr.) contribution and for background the residual growth and decay curve may be expressed by

$$A_2 - A_1{}^0\frac{\lambda_2}{\lambda_2-\lambda_1}e^{-\lambda_1 t} = \left(A_2{}^0 - A_1{}^0\frac{\lambda_2}{\lambda_2-\lambda_1}\right)e^{-\lambda_2 t}. \quad (1)$$

TABLE I.

MeBr cm	HBr cm	$A_1{}^0$	$A_2{}^0$	Efficiency
12	6	1328	−35	1.00
20	12	375	+15	0.96
15	0	1206	+45	0.96
45	45	2238	+30	0.99

The 4.5-hr. and 18-min. periods are adequately resolved and represented by

$$A_2 = A_1{}^0\frac{\lambda_2}{\lambda_2-\lambda_1}e^{-\lambda_1 t} \quad \text{for} \quad e^{-\lambda_1 t} \gg e^{-\lambda_2 t}, \quad (2)$$

$$A_2 + A_1{}^0\frac{\lambda_2}{\lambda_2-\lambda_1}\left(\lambda_1 t + \frac{\lambda_2{}^2 t^2}{2}\right) = A_1{}^0\frac{\lambda_2{}^2}{\lambda_2-\lambda_1}t + A_2{}^0, \quad (3)$$

during the time intervals 180–500 min. and 0–15 min., respectively. In these equations subscripts 1, 2 refer to parent and daughter and A, λ, t refer to activity, decay constant, and time, respectively. Table I summarizes these results. The experimental points agree with the expected slopes of both segments of the growth and decay curve in all cases.

It is interesting that even without addition of HBr there is very little apparent retention of Br^{80} (18 min.) by CH$_3$Br. Although no attempt was made to follow in detail the fate of daughter particles, it was repeatedly observed that about half of the 18-min. activity remained in the counter chamber after removal of the parent CH$_3$Br*. Unless the half-time for absorption of these particles is short, it might be expected that a time-dependent geometry would be exhibited as a trend in the 18-min. period. Since the latter is correct within the statistical counting error, the effect may be ignored since the conversion efficiency is based upon the ratio of extrapolated Br^{80} (18-min.) activities.

These experiments demonstrate that there is no branching decay of Br^{80} (4.5 hr.), that the chemical effects produced correspond to complete conversion, in agreement with the physical effects, and that quantitative correlation of chemical effects with nuclear phenomena in the liquid phase may be unreliable.

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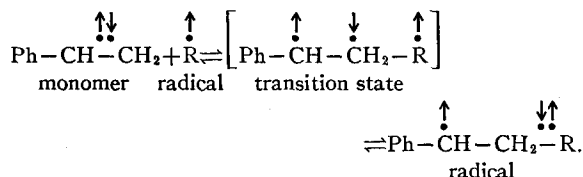
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Styrene Polymerization in a Magnetic Field

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SCHMID et al. have reported that a strong external magnetic field decreases the rate of the polymerization of styrene to methanol-insoluble polystyrene.[1] They suggest that the reaction impending influence of the magnetic field is due to the orienting of reacting molecules and the associated restriction of the mobility of the molecules. The Cotton-Mouton effect is probably too small at the temperature of polymerization of styrene to produce the observed decrease in rate by orienting the molecules. Since organic free radicals have been shown to be in a Σ-state[2] in which the coupling between the spin moment and the axis of figure of the molecule can be neglected, it is likely that an external magnetic field would orient not the radicals but only the spin moments of the odd electrons.

For the thermal polymerization of styrene, Walling has suggested that the rate is proportional to the first power of the rate constant of the radical propagation step.[3] Assuming that the chain propagation step in field-free space occurs by a preliminary uncoupling of the II-electrons, the process can be represented as follows:

$$\text{Ph}-\overset{\uparrow\downarrow}{\underset{\bullet\bullet}{\text{CH}}}-\overset{\uparrow}{\underset{\bullet}{\text{CH}_2}}+\overset{\uparrow}{\underset{\bullet}{\text{R}}}\rightleftharpoons\left[\text{Ph}-\overset{\uparrow}{\underset{\bullet}{\text{CH}}}-\overset{\downarrow}{\underset{\bullet}{\text{CH}_2}}-\overset{\uparrow}{\underset{\bullet}{\text{R}}}\right]$$

$$\underset{\text{monomer}}{} \underset{\text{radical}}{} \underset{\text{transition state}}{}$$

$$\rightleftharpoons\text{Ph}-\overset{\uparrow}{\underset{\bullet}{\text{CH}}}-\overset{\uparrow\downarrow}{\underset{\bullet\bullet}{\text{CH}_2}}-\text{R}.$$

$$\underset{\text{radical}}{}$$

In the presence of a strong external magnetic field the uncoupled state is more probably $\left[\text{Ph}-\overset{\uparrow}{\underset{\bullet}{\text{CH}}}-\overset{\uparrow}{\underset{\bullet}{\text{CH}_2}}-\overset{\uparrow}{\underset{\bullet}{\text{R}}}\right]$ where all three electron spin moments are now oriented with respect to the external field. Such a configuration would not lead to bond formation in either direction.

It is evident that this formulation agrees with the observed deceleration by the external magnetic field. If in the thermal depolymerization of polystyrene, degradation of a radical is involved, the same uncoupled transition state should occur, and an external magnetic field should diminish the rate constant of the radical degradation step.

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The Estimation of the Hindering Potential Barrier of Hexachloroethane by Electron Diffraction Investigation

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RECENTLY J. Karle[1] calculated the contribution of hindered rotation to electron diffraction by gaseous molecules and suggested that the hindering potential barrier V_0 of hexachloroethane for the rotation of CCl_3 groups would be determined by electron diffraction investigation, because the intensity curve of this molecule is sensitive to V_0/kT.

One of the present authors and his co-workers[2] interpreted the electron diffraction pattern of hexachloroethane by the rigid staggered model. Their treatment has an imperfection that the intensity relation between the 5th, 6th, and 7th maxima in the theoretical intensity curve do not agree with the observed pattern. It should be of great interest to remark that this disagreement can be removed by considering the effect of the hindering rotation of CCl_3 groups by Karle's method.

The curve V in Fig. 1 is the visual curve of the photograph obtained at room temperature, the curve A is the one which is calculated for the rigid staggered model, and the curve B is the one calculated at room temperature for
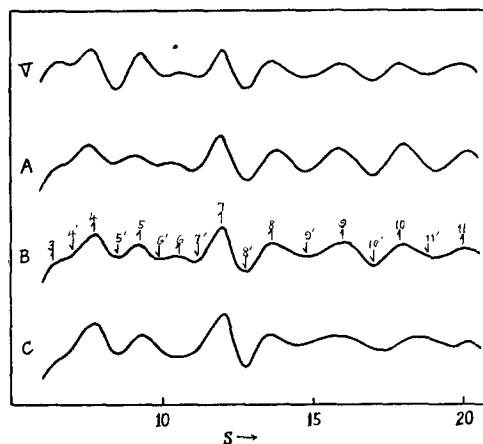

FIG. 1. Comparison of the theoretical intensity curves with the visual curve of hexachloroethane. Curve V, the visual curve; Curve A, the calculated curve for the rigid staggered model ($V_0=\infty$); Curves B and C, the calculated curve for the model of hindered rotation with $V_0=14$ and 6 kcal./mol., respectively. (The structure parameters used: $C-C=1.54A$, $C-Cl=1.77A$, and $\angle ClCCl=108° 45'$.)

the model of hindered rotation with $V_0=10$ kcal./mol. $\times(V_0/kT=17)$. The intensity curve between the 5th and 6th maxima is very sensitive to the barrier height. The diffraction pattern shows that the 6th maximum is very weak compared with the 5th and 7th maxima. But in the intensity curve for the rigid staggered model, both the 5th and 6th maxima are weak compared with the 7th maximum. When the effect of hindering rotation is taken into consideration, with decreasing the value of V_0/kT, the 5th maximum increases, while the 6th maximum decreases and disappears for V_0/kT smaller than 12. The features of the intensity curve between the 5th and 7th maxima agree well with the observed pattern at the value of $V_0/kT=17-25$. From this result the barrier height of hexachloroethane is estimated to be 10–15 kcal./mol.

The structure parameters which were determined by considering the effect of hindering rotation are as follows: $C-Cl=1.77\pm0.02A$, $C-C=1.54\pm0.07A$ and $\angle ClCCl=108° 45'\pm1° 30'$.

I. Miyagawa[3] in our laboratory computed the interatomic potential between chlorine atoms,

$$V=-1.515\times10^{-10}/r^6+1.620\times10^{-7}/r^{12} \text{ erg/molecule}$$

$$(r \text{ in A unit}),$$

from the second virial coefficients of the gas. By assuming that this function can also be applied to intramolecular potential, the hindering potential barrier of hexachloroethane is calculated to be 12 kcal./mol., which agrees with the observed value stated above.

For the determination of potential barrier it is desirable to study the temperature variation of the diffraction pattern of hexachloroethane, and we are now undertaking the experiment.

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