The Detection of Radioactive Persulfate Fragments in Emulsion Polymerized Styrene

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the heat of formation of $N_2O_5(c)$ to be 9.6 kcal. per mole, and for the following reaction (at 25°C)

$$N_2O_5(g) \rightarrow NO(g) + NO_2(g) + O_2(g)$$

$$\Delta H = +25.5 \text{ kcal.} \quad \Delta E = \Delta H - 2RT = +24.3 \text{ kcal.}$$

It is proposed that the apparently first-order decomposition of N_2O_5 is in reality a chemically complex process involving the transient intermediate NO_3—a well-recognized substance which plays an important role in related reactions.[3] Steps of the suggested mechanism follow, with indicated rate constants.

$$\begin{aligned}
&(1) \quad N_2O_5 \rightarrow NO_3 + NO_2 \quad k_1 \\
&(2) \quad NO_3 + NO_2 \rightarrow N_2O_5 \quad k_2 \\
&(3) \quad NO_3 + NO_2 \rightarrow NO_2 + O_2 + NO \quad k_3 \\
&(4) \quad NO + N_2O_5 \rightarrow 3NO_2 \text{—rapid}
\end{aligned}$$

The rate constant k_2 would be expected to be similar in magnitude to that for the corresponding recombination of NO_2 radicals—known to have at most a very small activation energy.[3] However, it will appear that reaction (3) is endothermic, and hence has appreciable activation energy. Consequently, at relatively low temperatures (~25°C), $k_3 \ll k_2$. By the usual "steady-state" treatment one finds

$$-\frac{d(N_2O_5)}{dt} = 2\frac{d(NO)}{dt} = 2\frac{k_1k_3}{k_2+k_3}(N_2O_5) \sim 2\frac{k_1}{k_2}k_3(N_2O_5).$$

The apparent first-order rate constant is thus in reality the product of an *equilibrium* constant (k_1/k_2) and a *second-order* rate constant (k_3). Hence no "falling off" of constants at low pressures is to be expected. The exhaustive experimental tests[3] have shown this to be the case—a fact for which no reasonable explanation could be offered on the basis of the collisional activation theory of first-order reactions.

The proposed quasi-equilibrium dissociation of N_2O_5 is supported by the observations of Ramsperger and Tolman[4] that at extremely low concentrations the ratio of final to initial pressures falls considerably *below* the value 2.5 corresponding to the reaction $N_2O_5 \rightarrow 2NO_2 + \frac{1}{2}O_2$. The data of these authors allow one to estimate rough values of the equilibrium constants for the dissociation $N_2O_5 \rightleftarrows NO_3 + NO_2$. If the corresponding entropy change is assumed to be similar to those for N_2O_4 and N_2O_3 dissociation, the dissociation energy is estimated very approximately as some 18–22 kcal. per mole (compare 14.0 and 9.7 for N_2O_4 and N_2O_3, respectively[5]).

The revised thermochemical values supply the strongest support of the proposed mechanism. Denoting reaction energies as "E," activation energies as "Q," and experimental values by the subscript "Ex," since

$$k_{Ex} = 2(k_1/k_2)k_3, \quad Q_{Ex} = E_1 + Q_3.$$

However, if (3) is endothermic by amount E_3, $Q_3 \geqq E_3$ and hence $Q_{Ex} \geqq E_1 + E_3$. Adding (1) and (3) and applying Hess' Law

$$N_2O_5 \rightarrow NO + NO_2 + O_2 - E_1 - E_3.$$

From the above new data, $E_1 + E_3 = 24.3$ kcal.—as compared with $Q_{Ex} = 24.6$ kcal. The near identity of these values suggests that Q_3 exceeds E_3 by very little. If E_1 is taken roughly as ~20 kcal., Q_3 is thus ~5 kcal.—a value sufficient to ensure the inequality $k_3 \ll k_2$.

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The Detection of Radioactive Persulfate Fragments in Emulsion Polymerized Styrene

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PRICE and co-workers[1] have shown that fragments of organic peroxide catalysts are chemically combined with polystyrene polymerized in oil phase. It is a much more difficult problem to demonstrate by chemical analysis the presence in the polymer of fragments of the inorganic peroxides normally used as catalysts in emulsion polymerization because of the high molecular weights of the polymers produced in emulsion in the absence of chain transfer agents. However, by the use of potassium persulfate prepared from radioactive S^{35} it has now been found that fragments (containing sulfur) of the potassium persulfate used as a catalyst in the emulsion polymerization of styrene are chemically combined with the polystyrene.

Radioactive potassium persulfate was prepared by electrolysis of potassium sulfate in sulfuric acid containing radioactive S^{35}. The radioactive S^{35} was received as a trace constituent of potassium chloride supplied by the Clinton Laboratories of the Monsanto Chemical Company.

The active potassium persulfate was used as a catalyst in polymerizing styrene in a soap emulsion. The polystyrene produced was purified by precipitating it from the emulsion with methyl alcohol, then dissolving in benzene and reprecipitating with methyl alcohol, the dissolving and reprecipitating being done three successive times. The polystyrene was then examined for radioactivity with a Geiger counter of the end window type.[2]

The background count was 2.5 counts per sec. A 0.1-mg sample of the potassium persulfate dried from solution in an aluminum dish gave a count of 480 $sec.^{-1}$. A sample of 50 mg of the purified polystyrene gave a count of 65.9 $sec.^{-1}$. An additional purification of the polystyrene by precipitating from benzene with methyl alcohol left the activity substantially unchanged, i.e., the count obtained was 65.3 $sec.^{-1}$.

Thus, sulfur containing fragments of the persulfate must be chemically combined with the polystyrene. We are now endeavoring to obtain the quantitative relation between persulfate fragments and number of polymer molecules.

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