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Sodium Resonance Radiation and the Polymerization of Ethylene

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Ethylene has been found to quench the resonance radiation of sodium between 130 and 250°C. No measurable polymerization of ethylene results as a consequence of quenching, in contrast to previous results with excited mercury and cadmium. A catalytic polymerization of ethylene at sodium surfaces occurs above 250°C with an activation energy of 20 kcal. The inefficiency of the energy of sodium resonance radiation in producing polymerization is ascribed to unfavorable localization of the energy received by ethylene in the quenching process.

IT is known that the polymerization of ethylene can be accelerated by both excited mercury¹ and cadmium² by using the resonance radiation of these elements as exciting radiation. With mercury this occurs at room temperature; with cadmium around 200°C. Thermally, polymerization may be secured at temperatures in the neighborhood of 350–400°C with an observed activation energy of 35–42 kcal.^{3, 4} Quite recently the subject of ethylene polymerization has acquired a new interest by reason of the demonstration that it is a chain reaction that can be brought about by the production in the ethylene system, at temperatures of 200–300°C, of free radicals; for example by thermal decomposition of metal alkyls⁵ and azomethane,⁶ or by photo production of free radicals.⁷ It was, therefore, of interest to test the effect of the resonance radiation of sodium as exciting agent, in an ethylene system containing sodium vapor. The choice of this source of energy derives its interest from the magnitude of the energy quantum involved ($\lambda = 5897\text{\AA}$; $E = 48$ kcal.) since this energy is greater than the necessary thermal activation energy but too small of itself or even with the accompanying formation of sodium hydride ($Q_{\text{NaH}} = 12.1$ kcal.) to effect the breaking of a carbon-hydrogen linkage thus producing a free radical.

We have, accordingly, studied the effect of ethylene on the quenching of sodium resonance

radiation, the rate of polymerization of ethylene in presence and absence of such radiation and also a polymerization which occurs in somewhat higher ranges of temperature due to the presence of sodium surfaces or vapor in such reaction systems.

EXPERIMENTAL

Light source

As source of resonance radiation we have used the commercial Zeiss sodium lamp of the standard type used in polarimetric and other optical work. The lamp operates on a 110-volt a.c. circuit with suitable external resistance, at 1.3 amperes. We have used such lamps for illumination periods of many hours with good satisfaction. While we have made no quantitative measurements of light intensity, visual observation showed a reasonable constancy of this light source.

Reaction system

We have used a Pyrex reaction system, the actual reaction vessel a cylinder 10 cm long by 2 cm diameter, fitted with suitable manometric device and pump system for evacuation. Into the reaction vessel, after a standard high temperature exhaustion, the sodium metal was introduced by distillation and formed on the walls of the vessel a bright metallic mirror. Large amounts of the metal were always present. The temperature of the reaction system was controlled by means of suitable vapor baths in Pyrex tubes surrounding the reaction space. The ethylene used was obtained from cylinders, passed through a carbon dioxide-ether trap and purified before use by several fractional condensations in liquid air with removal of permanent gases by evacuation. In all cases the gas

¹ Olson and Myers, *J. Am. Chem. Soc.* **48**, 389 (1926); Bates and Taylor, *ibid.* **49**, 2438 (1927).

² Bates and Taylor, *J. Am. Chem. Soc.* **50**, 771 (1928).

³ Pease, *J. Am. Chem. Soc.* **53**, 613 (1931).

⁴ Storch, *J. Am. Chem. Soc.* **56**, 374 (1934).

⁵ Taylor and Jones, *J. Am. Chem. Soc.* **52**, 1111 (1930).
⁶ O. K. Rice and Sickman, *J. Am. Chem. Soc.* **57**, 1374 (1935).

⁷ Taylor and Emeleus, *J. Am. Chem. Soc.* **53**, 562 (1931).

was condensed onto bright metallic sodium before introduction into the reaction system, in order to minimize still further the possible oxygen concentration.

Quenching of resonance radiation by ethylene

Upon illumination of the heated reaction tube containing sodium and its vapor alone with the light from the resonance lamp the whole vessel became suffused with the characteristic yellow glow of the resonance radiation. This glow was especially striking in the temperature region of 150–200°C. At the temperature of boiling diphenyl (255°C) the concentration of sodium vapor is already sufficiently high that complete absorption occurs in the layers immediately adjacent to the lamp and the fluorescence is localized. Under conditions in which the glow is especially pronounced, the admission of even 5 mm of ethylene sufficed to extinguish the fluorescence as observed visually. Such experiments sufficed to indicate (a) the emission of resonance radiation from the lamp source and (b) the transfer of the energy to ethylene by collision.

Photo-polymerization experiments

The following Table I records the conditions under which the polymerization of ethylene under the influence of resonance radiation was attempted. In no case, between the reaction temperature limits of 132 and 255°C, was any acceleration of the polymerization by photosensitization observed. The results were uniformly negative nor was any "permanent" gas, showing a pressure at liquid-air temperatures, produced during the several runs.

Even at a pressure of 133 mm recorded in run 5 the only pressure diminution recorded can be accounted for by the thermal reaction discussed in the succeeding section. An attempt to study the sensitized polymerization in presence

TABLE I. *Photosensitized polymerization of ethylene by sodium resonance radiation.*

RUN No.	TEMP. (°C)	PRESSURE (mm at 25°C)	TIME OF ILLUMINATION (Hours)	PRESSURE CHANGE (mm)
1	132	3.3	1.66	<0.1
2	184	4.8	10	<0.1
3	218	5.2	5.5	<0.1
4	255	5.25	5	<0.05
5	255	133	20	~1

TABLE II. *Thermal polymerization of ethylene in Pyrex vessels with and without a coating of sodium.*

RUN No.	TEMP. (°C)	PRESSURE (mm)	ΔP (mm)	Δt (hours)	$\Delta P/\Delta t$	REMARKS
1	302	182	20.6	44	0.46	Sodium Present
2	302	154.8	26.4	63	0.42	Sodium Present
3	302	167	2.4	38	0.06	Sodium Absent
4	354	166	1.0	23	0.04	Sodium Absent
5	354	180	22.0	17	1.3	Sodium Present
6	354	183	26.5	22	1.2	Sodium Present
7	302	184	23.8	70	0.34	Sodium Present
8	354	182	30.3	21	1.4	Sodium Present
9	255	181	23.0	232	0.1	Sodium Present

of hydrogen or the sensitized hydrogenation of ethylene is prevented by the ready reaction of sodium and hydrogen, in which respect this agent differs from the previously studied cases of mercury and cadmium.

Catalytic polymerization of ethylene

It was thought that sodium vapor might be an efficient agent for the removal of traces of oxygen from ethylene gas and that, therefore, the thermal polymerization of ethylene might be reduced thereby, since, as is well known, traces of oxygen accelerate the polymerization process.⁸ A series of experiments on the rate of thermal polymerization carried out in reaction vessels coated with a bright metallic sodium deposit are recorded in Table II.

Comparison of Experiments 3 and 4, in the absence of sodium, with the others in presence of sodium shows a marked accelerating influence on polymerization due to the presence of sodium. Experiment 9 indicates that the influence is measurable already at 255°C and accounts for the observed pressure change in the photosensitization experiment No. 5 of Table I under similar temperature and pressure conditions. That the influence of the sodium is catalytic is evident from the activation energy of the process. From Experiments 6, 7 and 8 we deduce $E=20$ kcal. The less accurate combination of Experiments 7 and 9 gives $E=17$ kcal. These values are much lower than the accepted value for thermal polymerization of 35–42 kcal.^{3, 4} This catalytic reaction makes difficult the study of photosensitization in the higher temperature ranges, but illumination with resonance radiation in this temperature interval produced no noticeable acceleration.

⁸ Lenher, J. Am. Chem. Soc. **53**, 3752 (1931).

DISCUSSION

The absence of any polymerization of ethylene photosensitized by sodium diminishes markedly any expectation that examples of photosensitization using sodium will be found. Acetylene and hydrogen both react with sodium vapor and many other common reactants are similarly reactive towards sodium. It would seem, therefore, that there is little prospect of extending the list of atom-photosensitized reactions to this element.

The quenching of the sodium resonance radiation by ethylene indicates definitely that in the collisions with ethylene, at least 48 kcal. of energy per mole are transferred to the ethylene molecules. Although this is a larger energy than that required as activation energy in the thermal polymerization process no observable polymerization results. This is another example of the relative efficiency of thermal activation as compared with photoactivation. The negative result in this photosensitization confirms the view resulting from the studies with mercury and cadmium as activating agents that the efficiency of these latter is to be associated with their ability to produce, in the reaction system, free radicals which are efficient agents in the initiation of a polymerization chain. With respect to the optical

and thermal methods of securing a particular reaction it should be observed that the method of calculation of activation energy in thermal processes takes account only of those collisions which, having the necessary activation energy, are successful, whereas, in the photosensitization studies, all the collisions are counted whether the energy is favorably located for reaction or not. Hence the lower apparent efficiency of light energy; hence, also, the observation that in thermal processes many collisions may occur with the necessary activation energy but unfavorable in the location of the activation. It is significant in this regard that Pease³ computed from his data that the A factor in the velocity equation $Ae^{-E/RT}$ was of the order of 0.001 of that to be expected of a straight bimolecular process and that the existence of a chain of any marked length would cause a still greater discrepancy between the actual and theoretical magnitudes of A . These considerations do not, however, exclude the possibility that the activation energy deduced from thermal data may have a low value due to a reaction of ethylene with another substance of unknown nature, which reaction provides for the initiation of the chain. To this extent the thermal polymerization process is still obscure.

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The Homogeneous Unimolecular Decomposition of Gaseous Alkyl Nitrites

V. The Decomposition of Methyl Nitrite at Low Pressures

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(Received November 19, 1935)

The decomposition of methyl nitrite has been investigated from 0.005 to 5.0 cm in the temperature range 210–240°C. In this region the rate falls off steadily with diminishing pressure. The reaction is appreciably heterogeneous at the lower pressures. The results are in satisfactory agreement with the previous observations of Steacie and Shaw at higher pressures. The falling-off in rate with decreasing pressure is satisfactorily accounted for by the Rice-Ramsperger theory, assuming 13 degrees of freedom and a molecular diameter of 5.0×10^{-8} cm.

INTRODUCTION

IN previous papers it has been shown that the decompositions of the gaseous alkyl nitrites constitute a series of simple first order reactions.¹

¹ Steacie and Shaw, (I) *Proc. Roy. Soc.* **A146**, 388 (1934); (II) *J. Chem. Phys.* **2**, 345 (1934); (III) *ibid.* **3**, 344 (1935); (IV) *Proc. Roy. Soc.* **A151**, 685 (1935).

Recently Rice and Herzfeld² have suggested that the majority of first-order reactions may really be chain processes involving free radicals, and in a number of cases their suggestion has received striking experimental confirmation. A large

² Rice and Herzfeld, *J. Am. Chem. Soc.* **56**, 284 (1934).