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M. K. Phibbs, B. de B. Darwent, and E. W. R. Steacie

crease again points to a cubic term in the energy expression. Neglecting this, the anharmonic term x_{14} comes out to be approximately 28 cm^{-1}. However, this anharmonic coefficient does not represent very well bands of the type $v_1v_1+v_4$ and $v_1v_1+3v_4$. This is probably because the observed bands $v_1v_4+2v_4$ are parallel bands, having the A_1 component level as upper state while the bands $v_1v_1+v_4$ are perpendicular bands, the upper state having the species E only. For $v_1v_1+3v_4$ the situation is more complicated.

The vibrational data here obtained are not sufficient to determine all the anharmonicity coefficients x_{ik}. Since, in addition, the effect of cubic terms and of Fermi resonance is difficult to take into account accurately at the present stage, we give in the last column of Table VI, for all bands other than those just discussed, the wave numbers computed by simply adding to the observed wave numbers of the bands of type v_1v_1 and $v_1v_1+2v_4$ the fundamental or sum of fundamentals involved according to the assignments given.[11] On account of the effect of anharmonicity and the other reasons mentioned above, one should not expect a very close agreement of calculated and observed wave numbers.

[11] See footnote (g) of Table VI.

The only reason for listing the calculated values is as support for the assignments given in the third column.

The central branches of the strong photographic bands are accompanied by weaker companions which must clearly be interpreted as difference bands of the type $v+v_i-v_i$ in which a low frequency fundamental is excited in both upper and lower state of the main band. Their positions relative to the main band are determined by the anharmonicity constants and cannot be predicted.

We are greatly indebted to Dr. A. F. Benning of the Jackson Laboratory of E. I. du Pont de Nemours and Company for putting at our disposal the fluoroform used in this investigation. Grateful thanks are due Dr. G. P. Kuiper for his cooperation in taking the infra-red spectra of fluoroform with his new photoelectric infra-red spectrometer. We also wish to thank Dr. W. C. Price for letting us have his data about the fundamentals of CHF$_3$ in advance of publication. Finally, we would like to express our appreciation to Professor R. W. Wood for supplying us with the remarkable grating with which the high resolution work was carried out.

The Mercury Photosensitized Reactions of Ethylene Oxide*

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The reactions of ethylene oxide with Hg($^3P_1$) atoms have been investigated at 25°C at pressures between 10- and 600-mm Hg, and at 200°C and 300°C at 100-mm Hg. The principal products are H$_2$, CO, CH$_3$CHO and a polymer; smaller amounts of CH$_4$, C$_2$ hydrocarbons and formaldehyde are also formed. The nature of the products and the very small effect of pressure on the reaction are best explained by a mechanism based principally on the formation of the activated ethylene oxide molecule, with a minor portion of the reaction proceeding via a C—H split.

INTRODUCTION

THE reactions between Hg($^3P_1$) atoms and the lower hydrocarbons have been studied in some detail.[1] It appears that, in general, the unsaturated hydrocarbons react principally by the transfer of energy from the excited mercury

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[1] See E. W. R. Steacie, *Atomic and Free Radical Reactions* (Reinhold Publishing Corporation, New York, 1946).

atom to the hydrocarbon molecule, leading to the formation of an excited hydrocarbon from which the products arise; on the other hand, the saturated hydrocarbons appear to react by a direct C−H split, which may or may not involve the formation of HgH, leading to the formation of the corresponding alkyl radical and an H atom. It has recently been shown that diethyl-ether[2] probably reacts with Hg($^3P_1$) atoms in a manner similar to the paraffins, whereas acetone[3] appears to behave like the olefins, and to react by the transfer of energy. The mercury photo-sensitized reactions of ethylene oxide are of interest in connection with the photo-chemical reactions of the simple oxygen containing organic compounds, since the oxygen atom may form part of a ring structure.[4]

EXPERIMENTAL

The ethylene oxide used was obtained from the Matheson Company, East Rutherford, New Jersey. It was used after repeated melting and freezing in vacuum followed by a simple bulb to bulb distillation. No impurities were detectable by the analytical methods used. The absorption spectrum was checked at atmospheric pressure on a Beckmann quartz spectrophotometer (10-cm path), and it was found to be completely transparent to 2200A.

The reaction was investigated in a circulatory system in which all of the ethylene oxide was present in the gas phase, no attempt being made to remove the higher boiling products of the reaction by means of cold traps since very small conversions were used. The gases were circulated by means of a pump of the type described by Puddington[5] over warm mercury, through a mercury desaturator and a cylindrical quartz vessel with plane ends in which the reactants were illuminated with the unfiltered light from a low pressure mercury lamp with neon (3 mm) as carrier gas. Since the incident light traveled through a distance of about 12 inches in air, it is reasonably certain that only traces of λ1849 could have reached the reactor.

The products of the reaction were separated by pumping off a trap kept successively at −183°, −126°, and −80°C. The products volatile at −183°C (H₂, CO, and CH₄) and at −126°C (C₂ hydrocarbons) were analyzed by conventional methods. The residual ethylene oxide (volatile at −80°C) was estimated by $P−V$ relations and by titration as recommended by Lubatti.[6] Specific tests showed formaldehyde[7] to be absent from the C₂ (−183° to −126°C) fraction but to be present in the "ethylene oxide" fraction. Acetaldehyde was also found[8] in the "ethylene oxide" fraction in which it was estimated by the sodium bisulfite—iodine—sodium thiosulfate titration[9] after correction for formaldehyde which was estimated colorimetrically.[10] A small blank correction was necessary when acetaldehyde was estimated after the titration for ethylene oxide. The correction was negligible and the reproducibility better when the ethylene oxide titration was omitted; in these cases the residual ethylene oxide was determined by $P−V$ relation by correcting for the total aldehyde present. No detectable pressure developed on allowing the trap to warm up, after removal of ethylene oxide, from −80° to room temperature.

A non-volatile white solid was visible on the walls of the reaction vessel at the end of each experiment at room temperature. It was also found that under these conditions a large proportion of the ethylene oxide reacted could not be accounted for by the gaseous products and aldehydes. Accordingly, experiments were conducted in a single-pass system to obtain enough of the heavy products for identification. In these experiments a much more intense light source was used and the flow rate of the ethylene oxide adjusted to permit 10–20 percent reaction per pass. No white solid was deposited on the walls, but droplets of a relatively high boiling liquid appeared early in these experiments. The products obtained

[2] B. de B. Darwent, E. W. R. Steacie, and A. F. van Winckel, J. Chem. Phys. 14, 551 (1946).

[3] E. W. R. Steacie and B. de B. Darwent, unpublished.

[4] For opinions on the structure of ethylene oxide see, however, P. V. Zimakov, J. Phys. Chem. (U.S.S.R.) 20, 133 (1946); A. D. Walsh, Nature 159, 165, 712 (1947); R. Robinson, ibid. 159, 400 (1947), 160, 162 (1947).

[5] I. E. Puddington, Ind. Eng. Chem. (Anal. Ed.) 17, 592 (1945).

[6] O. F. Lubatti, J. Soc. Chem. Ind. 54, 424 (1935).

[7] S. B. Schryver, Proc. Roy. Soc. (London) 82B, 226 (1910).

[8] A. Ley, J. pharm. chim. (6) 22, 107 (1897).

[9] I. M. Kolkoff and N. H. Furman, Volumetric Analysis (John Wiley and Sons, Inc., New York, 1929), Vol. II, p. 450.

[10] D. Matukawa, J. Biochem. (Tokyo) 30, 386 (1939).

from one experiment separated on cooling into two layers, the upper of which boiled at about 165°C and the lower at about 99°C. Fractional distillation of the products of further experiments gave three fractions, the identifications of which were unsuccessful, but tests showed them to be aldehydic in nature and showed the absence of such plausible compounds as dioxanes, dioxolanes, 1,3-diepoxybutane, and alcohols. The white polymer produced in the low intensity circulating runs was found to be water soluble and aldehydic in nature; it was easily removable from the walls by warming or by flaming in an oxygen atmosphere, the latter being the procedure adopted for cleaning the cell before each run. It is worthy of note that this white polymer was not formed on the incident face, but rather on the cylindrical side walls of the cell, and started about 1 mm from the incident face.

Some experiments were carried out at higher temperatures. In these runs the quartz reactor was enclosed in a furnace fitted with a quartz window. All other conditions were unaltered. No visible polymer was formed in these experiments, and the material balance was satisfactory at 200°C and higher temperatures.

The light intensity was measured by the rate of hydrolysis of monochloracetic acid (0.5N) in the cell. The corrections as given by Smith, Leighton, and Leighton[11] for the dark reaction were applied.

RESULTS

Details of the experimental conditions and results on which subsequent discussion will be based are given in Table I. From these results it is evident that the rates of production and composition of the gaseous products at any given pressure are independent of time. The data for the amount of ethylene oxide reacted are much more variable, being small differences of two large quantities, but the rate here may also be taken as independent of time within the limits of accuracy of the determination. The rate of production of aldehydes is not independent of time (Fig. 1); however, it seems likely that the initial rate of production of aldehydes is approxi-

[11] R. N. Smith, P. A. Leighton, and W. G. Leighton, J. Am. Chem. Soc. 61, 2299 (1939).

mately independent of the initial pressure of ethylene oxide. By basing the discussion on the initial rates the complications connected with

TABLE I. The mercury photosensitized decomposition of ethylene oxide.

Experimental conditions and results
Volume of system—726 cc, λ2537 absorbed—9.82×10⁻⁵ einstein/hr.
Volume of reaction vessel—230 cc, Hg pressure, 1.2×10⁻³ mm.
Circulation rate—400 cc/min. at prevailing pressure.

I. Experiments at room temperature—25±2°C

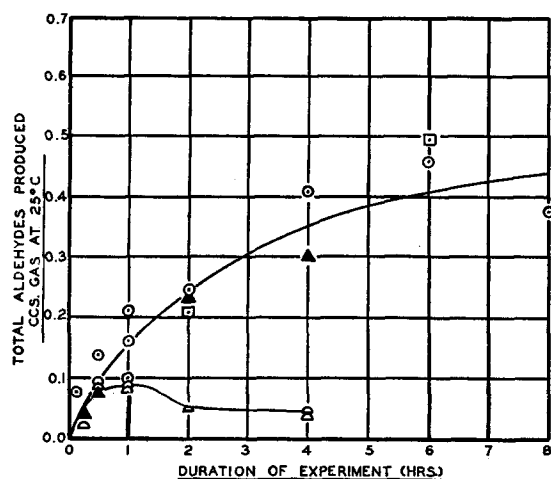| Expt. No.	Duration, hours	Ethylene oxide reacted cc 25°C	H₂	CO	CH₄	C₂	Total ald.
A. Initial pressure of ethylene oxide = 10±1 mm							
29	1.0	0.5	0.27	0.46	0.09	0.16	—
28	2.0	1.8	0.48₅	0.92	0.19	0.28	—
33	5.1	2.4	0.98₅	1.91	0.39	0.52	—
B. Initial pressure of ethylene oxide = 40 mm							
44	0.25	—	—	—	—	—	0.05
45	0.5	—	—	—	—	—	0.16
9	0.5	0.5	0.19	0.26	0.05	0.08	0.18
3	1.0	1.7	0.38	0.58	0.10	0.15	0.16
46	1.0	—	—	—	—	—	0.16
1	2.0	2.5	0.72	1.06	0.20	0.33	0.10
2	4.0	3.9	1.36	2.04	0.37	0.55	0.07
11	4.0	—	—	—	—	—	0.09
C. Initial pressure of ethylene oxide = 100 mm							
43	0.25	—	—	—	—	—	0.10
32	0.25	0.6	—	—	—	—	—
42	0.5	—	—	—	—	—	0.15
25	1.0	2.2	0.39	0.52	0.09	0.12	—
41	2.0	—	—	—	—	—	0.47
23	4.0	5.2	1.52	2.00	0.32	0.46	—
40	4.3	—	—	—	—	—	0.61
24	8.0	8.88	2.78	3.57	0.59	0.66	—
D. Initial pressure of ethylene oxide = 200 mm							
14	0.17	—	—	—	—	—	0.15
10(A)	0.5	—	0.21	0.24	0.05	0.08	—
12(A)	0.5	—	—	—	—	—	0.27
8	1.0	1.7	0.42	0.48	0.09	0.11	0.20
11(A)	1.0	—	—	—	—	—	0.42
4	2.0	2.9	0.88	1.04	0.16	0.20	0.48
6	4.0	6.3	1.72	1.94	0.31	0.31	0.81
13	6.0	—	—	—	—	—	0.91
5	8.0	10.4	3.12	3.66	0.57	0.55	0.75
E. Initial pressure of ethylene oxide = 600 mm							
18	1.0	2.2	0.45	0.43	0.09	0.10	—
21	1.0	2.6	—	—	—	—	—
15	2.0	—	0.89	0.91	0.14	0.18	0.42
20	3.0	5.1	—	—	—	—	—
16	4.0	—	1.83	1.78	0.28	0.24	—
16(A)	6.0	9.7	2.57	2.42	0.37	0.42	0.99
22	10.0	12.9	4.48	3.94	0.67	0.64	—
II. Experiments at 200°C and an ethylene oxide pressure of 100 mm							
36	1.0	2.5	0.70	1.29	0.30	0.37	1.66
37	3.0	4.5	2.03	4.09	0.95	1.19	1.74
III. Experiments at 300°C and an ethylene oxide pressure of 100 mm							
38	1.0	3.1	0.85	2.03	0.71	0.53	1.57
38(A)	1.0	(Blank—lamp off—total non-condensible gas = 0.043 cc)					1.41

FIG. 1. The production of aldehydes at 25°C; initial pressure of ethylene oxide as follows: squares—600 mm; circles—200 mm; triangles—100 mm; half-circles—40 mm. (In experiments at 40, 200, and 600 mm the ethylene oxide was estimated by titration before the aldehydes were determined; the aldehyde content was less accurate than in the experiments at 100 mm in which no titration for ethylene oxide was attempted.

the disappearance of aldehydes in the later stages of the reaction may be eliminated.

The effect of pressure on the initial rates is shown in Table II. The data given here show that the gaseous and aldehydic products do not account for all the material reacted except at the lowest pressure. It has been mentioned previously that a white solid polymer was formed during the experiments. The effect of pressure on the rate of polymerization has been calculated (Table III) from material balances, and the results show the increase in the extent of the polymerization reaction with pressure. The composition of the polymer (ratios H/C and C/O) is given in columns 11 and 12 of Table III. The H/C ratio is constant, within experimental error, at 2.0 and is approximately independent of pressure, whereas the C/O ratio decreases, indicating in-

TABLE II. Effect of pressure on the mercury photosensitized decomposition of ethylene oxide at 25°C.

Initial pressure mm	A. Experiments at room temperature					
			Rates—cc/hr. (25°)			
	$-(CH_2)_2O$	H_2	CO	CH_4	C_2	ald.
10	0.56	0.21	0.42	0.082	0.118	0.45
40	1.02	.35	.53	.094	.145	.45
100	1.30	.36	.475	.076	.093	.45
200	1.44	.411	.47	.074	.081	.45
600	1.50	.445	.42	.070	.067	.45

creasing oxygenation, with increasing pressure. The above results and the fact that two immiscible liquids were found in the single-pass experiments lends plausibility to the suggestion that the total polymer consisted of two types of substance $((CH_2)_2O)_n$ and $(CH_x)_n$, in which X lies between 1.2 and 2.1 with an average value of 1.8, as shown in Table IV.

The effect of pressure is shown in Fig. 2 in which the rates given in Tables II and IV are plotted against the reciprocal of the pressure. The relationship between pressure and the rates shown in Fig. 2 for the experiments at room temperature is as follows:

$$\frac{d}{dt}(H_2) = 0.450 - \frac{5.5}{p},$$

$$\frac{d}{dt}(CO) = 0.425 + \frac{4.5}{p},$$

$$\frac{d}{dt}[((CH_2)_2O)_n] = 0.660 - \frac{25.0}{p},$$

$$\frac{d}{dt}(C_2) = 0.060 + \frac{3.1}{p},$$

$$\frac{d}{dt}(CH_4) = 0.064 + \frac{1.0}{p},$$

where the rates are in cc (25°C) per hour and p = pressure (mm Hg) of ethylene oxide. The lowest pressure investigated (10 mm) has not been included in Fig. 2 because the results indicate that quenching was incomplete below about 40 mm.

DISCUSSION

The following processes have been shown to occur in the mercury photosensitized reactions of ethylene oxide at room temperature:

(a) Isomerisation to acetaldehyde: the initial rate of production of acetaldehyde being independent of the ethylene oxide pressure.

(b) Decomposition to H_2, CO, CH_4, C_2 hydrocarbons and formaldehyde. The rates of production of the above substances (except formaldehyde) are linear functions of the reciprocal pressure such that the rates are finite even as $p \to \infty$, the pressure dependence in all cases being small.

TABLE III. Effect of pressure on the mercury photosensitized polymerisation of ethylene oxide at 25°C.

Pressure mm	Reaction rates cc atom/hr. (25°C)			Gases and aldehydes+ cc atom/hr. (25°C)			Polymer (by diff.) cc atom/hr. (25°C)			Comp. of polymer	
	C	H	O	C	H	O	C	H	O	H/C	C/O
10	1.12	2.24	0.56	1.52	2.92	0.87	−0.40	0.00	−0.31	—	—
40	2.04	4.08	1.02	1.70	3.38	0.98	0.34	0.70	0.04	2.1	8.5
100	2.60	5.20	1.30	1.52	3.04	0.92	1.08	2.16	0.38	2.0	2.8
200	2.88	5.76	1.44	1.48	3.08	0.92	1.40	2.68	0.52	1.9	2.7
600	3.00	6.00	1.50	1.40	3.09	0.87	1.60	2.91	0.63	1.8	2.5

+ The average composition of the aldehydes was 75 percent $CH_3 \cdot CHO$, 25 percent HCHO.

(c) Polymerization to yield substances of the types $((CH_2)_2O)_n$ and $(CH_2)_n$—the rate of production of the former being quite strongly pressure dependent, whereas the latter is approximately independent of pressure.

The occurrence of an isomerisation reaction, by which acetaldehyde is formed as a major product, and the pressure independence of that reaction, indicate that an active ethylene oxide molecule is formed in the primary act:

$$Hg(^1S_0) + h\nu_{2537} \rightarrow Hg(^3P_1), \qquad (0)$$
$$Hg(^3P_1) + (CH_2)_2O \rightarrow C_2H_4O^* + Hg(^1S_0), \qquad (1)$$
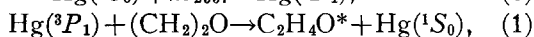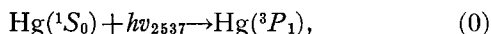
from which acetaldehyde is produced by either a first or second order process:

$$C_2H_4O^* \rightarrow CH_3CHO, \qquad (2)$$

$$C_2H_4O^* + (CH_2)_2O \rightarrow CH_3CHO + (CH_2)_2O. \qquad (2^1)$$

The above reactions (2) and (2^1) are energetically possible since the active molecule may possess as much energy as 112 kcal. per mole, and thermal investigations[12] indicate that only 52 kcal. per mole are necessary for isomerization. Any process by which acetaldehyde could be formed by atomic and/or radical recombination, providing that the atoms or radicals also react with

ethylene oxide, would lead to kinetics such that the rate of formation of acetaldehyde would be inversely proportional to the concentration of ethylene oxide.

The effect of pressure on the decomposition to hydrogen and carbon monoxide is also in agreement with the supposition that an active molecule plays the predominant role in the initial step of this reaction. If the decomposition were largely due to a $C-H$ split followed by "atomic cracking," the type of process frequently postulated to account for $C-C$ splitting in the photosensitized reactions of the paraffin hydrocarbons, it would be expected that, since H atoms react with ethylene oxide[13] at about the

TABLE IV. Effect of pressure on the composition of the polymer.

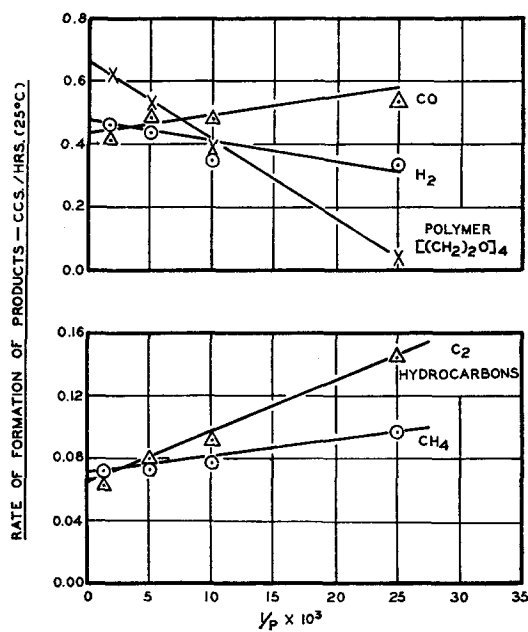| Pressure mm	cc $((CH_2)_2O)_n$ per hour	cc $(CH_x)_n$ per hour	X
10	—	—	—
40	0.04	0.26	2.1
100	0.38	0.32	2.0
200	0.52	0.36	1.7
600	0.63	0.34	1.2

FIG. 2. The effect of pressure on the decomposition and polymerization reactions at 25°C.

[12] W. W. Heckert and E. Mack, J. Am. Chem. Soc. 51, 2706 (1929).

[13] W. R. Trost and E. W. R. Steacie, unpublished.

same rate at room temperature as they do with the paraffins, the rate of decomposition would approach zero as the concentration of ethylene oxide approaches infinity. Since such a relationship has not been found, it must be concluded that a $C-H$ split cannot play an important role in the mechanism. The decomposition of the excited molecule may be first or second order:

$$C_2H_4O^* \rightarrow H_2 + CO + CH_2, \tag{3}$$

$$C_2H_4O^* + (CH_2)_2O \rightarrow H_2 + CO + CH_2 \\ + (CH_2)_2O. \tag{3^1}$$
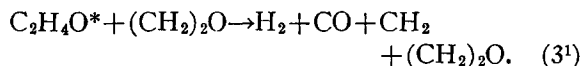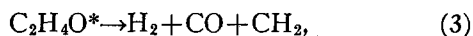
An alternative process by which the decomposition proceeds by virtue of acetaldehyde in the stable or activated state, such as was found for the thermal and H-atom reactions[13] of ethylene oxide, does not agree with the results of the present investigation. That type of process would lead either to an induction period or to a pressure dependence such that the rate of decomposition would approach zero at higher pressures.

If the excited molecule acquires almost all of the energy of the $Hg(^3P_1)$ atom (112 kcal. per mole), it will be possible for reactions (2^1) and (3^1) to occur in a single step leading to the isomerization of one molecule and to the decomposition of the other in the collision between one excited and one ground-state ethylene oxide molecule.

The results obtained do not allow of a choice between the first- and second-order processes outlined above. The limiting high pressure rates, obtained by extrapolation in Fig. 2, give the following quantum yields:

$$\phi \text{ Decomp.} = 0.18,$$
$$\phi \text{ Isom.} = 0.12,$$
$$\phi \text{ Polym.} = 0.36,$$
$$\phi \text{ Total} = 0.66.$$

Hence only 0.30 mole of ethylene oxide isomerizes or decomposes per einstein absorbed. This inefficiency may be due to either a first- or second-order process:

$$C_2H_4O^* \rightarrow (CH_2)_2O + h\nu \tag{4}$$

$$C_2H_4O^* + (CH_2)_2O \rightarrow 2(CH_2)_2O. \tag{4^1}$$
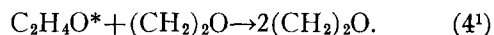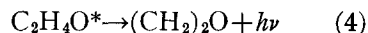
Since no investigation of fluorescence was made, it is not possible to decide between the alternatives since either a short-lived excited molecule with fluorescence or a long-lived one which on collision always either reacts or is deactivated will explain the results.

The very small effect of pressure on the rate of production of the minor products (CH_4, C_2 hydrocarbons and formaldehyde) indicates that they also arise in some way from the decomposition of the excited molecule.

The above mechanism accounts for the major characteristics of the isomerization and decomposition reactions but not for the pressure dependence, small though it is, of the decomposition. Also the fact that polymerization is important at high pressures, and that more hydrogen than carbon monoxide is formed at high pressures show that a small portion of the reaction probably proceeds by a free radical mechanism. The following type of process

$$Hg(^3P_1) + (CH_2)_2O \rightarrow C_2H_3O + H + Hg(^1S_0), \tag{1^1}$$
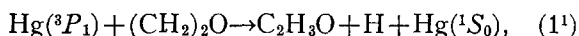
is well known in photosensitized reactions and is probably responsible for this aspect of the reaction. The nature of the polymer is consistent with the initiation of polymerization by the C_2H_3O radical, and the increase in "atomic cracking" with the decreasing pressure explains the small pressure dependence, providing that the major portion of the initial act is reaction (1) rather than (1^1). The effect of temperature can be explained by the decomposition of the C_2H_3O radical leading to increasing CO and decreasing polymer at high temperatures.