

[CONTRIBUTION FROM COATES CHEMICAL LABORATORY, LOUISIANA STATE UNIVERSITY]

## The Kinetic Decomposition of Ethyl Chlorocarbonate II. Foreign Gas Effects

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A study of the kinetics of decomposition of pure ethyl chlorocarbonate was published recently and the present report constitutes the second in this series. The effects of foreign materials on the rate constant have been considered in specific relation to their normal decomposition described in the previous report. The techniques employed were chosen to coincide as nearly as possible with those of the original investigation, thus minimizing errors of comparison.

The thermoregulation and reaction system were essentially as described in the previous article.<sup>1</sup> The reaction was investigated by a static method in an all-glass system. A glass diaphragm and an automatic pressure regulating device were used in following the rate of reaction.

### Experimental

Before the first run with any gas each reaction cell was thoroughly cleaned and flamed. A small bulb containing ethyl chlorocarbonate was first sealed into the cell and the foreign gas supply attached to the cell through a small side arm. The cell was then alternately evacuated and rinsed with the gas to displace adsorbed molecules of air and water vapor. The gas was next admitted to the desired pressure and the reaction vessel sealed. The vessel was finally brought to the temperature of the bath and the reactant bulb broken with the glass enclosed hammer.

When liquids of high vapor pressure were used as foreign materials a similar procedure was followed. However, when the vapor pressure was too low for the effective utilization of this method solutions of the liquid in ethyl chlorocarbonate were prepared. These solutions were chosen by composition to give approximately the desired partial pressure of each component, introduced into bulbs, and discharged in the cell in the usual way. The substances were tested thoroughly for chemical interaction before this procedure was employed.

In some cases the foreign substance was admitted at room temperature and the gas laws used to predict its partial pressure at reaction temperature. In other cases the foreign gas was allowed to come to temperature equilibrium before breaking the reactant bulb. Checks between the two methods showed the error to be negligible.

Oxygen, carbon dioxide, hydrogen and nitrogen were purified in conventional washing procedures for certain runs. They were not refractionated, however. Commercial carbon tetrachloride, hexane and benzene were subjected to careful fractionation. Nitric oxide was prepared according to the method of Johnston and Giaque<sup>2</sup> and

stored in a five-liter container. Because of the difficulty of separating nitric oxide from certain other oxides of nitrogen, particularly nitrous oxide, the effect of the latter compound on the reaction was investigated. For this purpose a cylinder of the commercial product was used without further purification.

### Experimental Results

As previously reported<sup>1</sup> the temperature 175° is approximately in the middle of the measurable range and gives rate constants of a convenient magnitude. This temperature was used for the greater number of runs on foreign gas effects. The effects of foreign materials on the rate were catalogued by comparison with the values for the specific rate constant  $k$  obtained in the previous research, and checked by controls during the present investigation. Where low pressure runs were made this effect was taken into account in tabulating the effect of foreign materials.

Runs were first made in the presence of an excess of carbon dioxide for the purpose of testing the reaction for reversibility. No measurable equilibrium effect could be detected. However, the carbon dioxide molecules seemed quite effective in maintaining the rate. No appreciable decrease in the value of  $k$  was detected as long as the total initial pressure remained above 175 mm.

Nitrogen and oxygen were also quite effective in maintaining the high pressure energy distribution. Curves showing typical rates of decomposition in the presence of these gases are shown in Fig. 1. Curves also have been included to show the effects of benzene, carbon tetrachloride and hexane. As may be seen from Table I, hexane increases the rate slightly while benzene and carbon tetrachloride show slight depressions. The effect is so slight that they may be regarded as relatively inert.

For many reactions hydrogen has been found quite effective in maintaining the rate at low pressures of reactant. In the case of ethyl chlorocarbonate, however, hydrogen fails to fulfill this function. It is less effective than any of the previously mentioned gases.

Chlorine exhibits a positive catalytic effect which does not seem to be directly proportional to the amount of chlorine present. Analyses of the products indicated no change in the nature of

(1) Choppin, Frediani and Kirby, *THIS JOURNAL*, **61**, 3176 (1939).

(2) Johnston and Giaque, *ibid.*, **51**, 3194 (1929).

TABLE I

$P_1$ (total)	$P_{\text{for. gas}}$	$K_{\text{obsd.}}$	$K_{\text{pure reas.}}$
Nitrogen			
124	30	0.040	0.034
148	120	.043	.037
200	65	.047	.045
236	25	.041	.045
175 <sup>a</sup>	51	.180	.183
Oxygen			
24	15	0.015	0.015
200	98	.043	.045
280	251	.041	.045
322	80	.047	.045
Carbon Dioxide			
102	45	0.030	0.030
285	178	.048	.045
286	206	.050	.045
83 <sup>a</sup>	25	.114	.11
Hydrogen			
131	57	0.029	0.036
146	98	.022	.037
337	294	.016	.045
386	327	.023	.045
Chlorine			
300	50	0.114	0.045
301	144	.099	.045
350	155	.106	.045
527	342	.117	.045
Water			
136	70	0.0816	0.036
151	14	.0781	.038
Nitrous Oxide			
68	50	0.019	0.026
125	60	.017	.033
168	35	.017	.039
225	111	.022	.045
268 <sup>c</sup>	101	.062	.089
Benzene			
200	104	0.029	0.044
493	133	.035	.045
Hexane			
108	54	0.052	0.031
164	82	.053	.039
Carbon Tetrachloride			
256	192	0.033	0.045
260	130	.038	.045
308	231	.035	.045
Nitric Oxide			
236	72	0.065	0.045
281	50	.057	.045
320	45	.055	.045
319	16	.046	.045
155 <sup>a</sup>	30	.098	.089

<sup>a</sup> Results of H. A. Frediani. <sup>b</sup> 195°. <sup>c</sup> 185°.

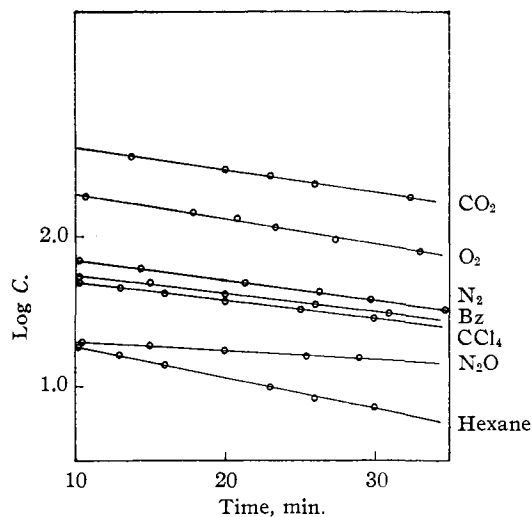


Fig. 1.

the reaction. It will be noted from Table I that the specific rate constant is more than doubled. The reaction definitely does not follow a first order rate over the first ten minutes. During this period the rate was more nearly second order with respect to the reactant. However, no good agreement for either was obtained over appreciable periods of time. Since the degree of catalysis does not seem to vary with the partial pressure of chlorine, one might conclude that the action takes place at the walls with adsorbed chlorine atoms acting as active centers. Thus a condition of saturated adsorption might govern the extent of catalytic action.

Ethyl chlorocarbonate is known to undergo both ammonolysis and hydrolysis. In the liquid state these reactions take place at the phase boundary, the reaction with aqueous ammonia proceeding quite rapidly and that with water at a much slower rate. At 175° the hydrolysis proceeds quite rapidly and the products slightly catalyze the thermal decomposition of any ethyl chlorocarbonate in excess. The presence of simultaneous reactions is apparent, and the initial stages can be described by neither a first nor second order rate. In view of the difficulty of separating these reactions the calculations of rate give at best a qualitative picture of the process, indicating principally the final effect of the bimolecular products upon the unimolecular reaction.

Inhibition by nitric oxide has been widely used as a test for one type of chain mechanism. Hinshelwood<sup>3</sup> has found low partial pressures quite

(3) Staveley and Hinshelwood, *J. Chem. Soc.*, 1568 (1937).

effective in suppressing the rates of a number of reactions proceeding through aliphatic free radical mechanisms. Pressures of nitric oxide of the order of 1 or 2 mm., suggested as being sufficient to seriously alter the reaction rate, were found to have no effect in the present case. As the partial pressure of nitric oxide was increased, however, a period of induction was observed. The length of the induction period varied with the partial pressure of nitric oxide (Fig. 2). At the end of the initial inhibition the reaction proceeded with a velocity greater than normal. Rate constants obtained for this region showed a consistent increase over normal values. Considering the high partial pressures of nitric oxide which caused this effect and the general unfavorable conditions for radical production, the indicated mechanism is some transient chemical interaction between the gas and the reactant. A catalytic effect of large partial pressures of nitric oxide has been observed in the decomposition of a number of compounds.<sup>4,5,6</sup>

In view of the difficulty of obtaining nitric oxide free from traces of nitrous oxide several runs were made with nitrous oxide to determine its effect on the reaction. Smooth curves were the result, with rates slightly depressed.

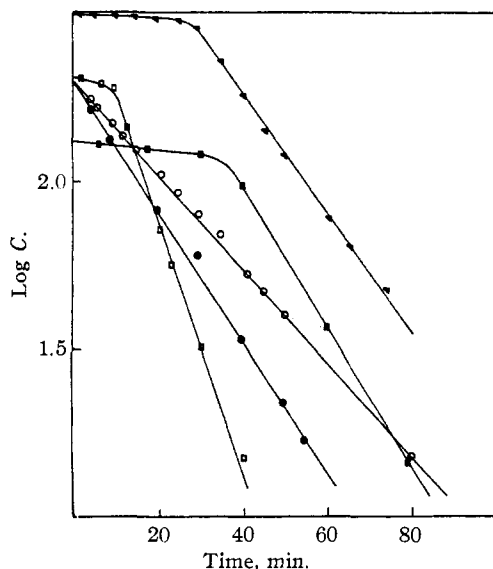


Fig. 2.—Effect of varying nitric oxide pressure;  $\nabla$ , 95 mm.;  $\square$ , 50 mm.;  $\blacksquare$ , 71.5 mm.;  $\bullet$ , 30 mm.;  $\circ$ , 16 mm.

### Discussion of Results

The observations cited above indicate a mecha-

(4) Staveley and Hinshelwood, *Proc. Roy. Soc. (London)*, **A164**, 335 (1936).

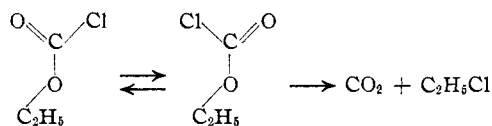
(5) Staveley and Hinshelwood, *J. Chem. Soc.*, 812 (1936).

(6) Daniels and Veltman, *J. Chem. Phys.*, **7**, 756 (1939).

nism of extreme simplicity. This conclusion was first strongly implied by the quantitative decomposition of ethyl chlorocarbonate to carbon dioxide and ethyl chloride. Chemical analyses of these products have been further supported by spectrographic investigations.<sup>7</sup> No evidence of chlorine or phosgene could be obtained. Furthermore, ethyl chlorocarbonate does not absorb in the visible and the first appreciable ultraviolet absorption occurs with a continuum beginning in the region of 2500 Å.

The temperature at which decomposition takes place and the low energy requirement seems to preclude the possibility of an initial disruption into unstable fragments since the activation energy is lower by at least 40,000 cal. than any of the minimum bonding energies that might be involved. In addition to this the wall effects are negligible, the reaction proceeds smoothly over a wide range of pressures and in most cases there is no marked inert gas effect.

These facts seem to point to a mechanism involving an internal rearrangement with the elimination of carbon dioxide. The structure of ethyl chlorocarbonate as established by dipole measurements is in accord with such a mechanism.<sup>8,9</sup> The following resonating structures have been proposed by earlier investigators:



The work being carried on in this Laboratory, it is hoped, will be of value in establishing the significance of any structural changes insofar as they affect the decomposition.

### Summary

The decomposition of ethyl chlorocarbonate has been investigated with regard to foreign materials. The products of the decomposition and a number of chemically inert gases are effective in maintaining the high pressure rate. The reaction is catalyzed by chlorine and, after a slight period of induction, by nitric oxide.

The kinetic results indicate a decomposition mechanism of a simple nature, probably involving an internal rearrangement with the elimination of carbon dioxide.

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(7) Unpublished data of C. H. Smith.

(8) Mizushima and Kubo, *Bull. Chem. Soc. Japan*, **13**, 174 (1938).

(9) Unpublished results of Robert E. Wood.