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E. W. R. Steacie

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Cross-Activation in the Unimolecular Decomposition of Mixtures of Gaseous Methyl and Ethyl Ether

E. W. R. STEACIE, *Physical Chemistry Laboratory, McGill University, Montreal*

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On account of the disagreement between previous investigations of Kassel and the writer, the decomposition of mixtures of methyl and ethyl ether has been reinvestigated with greater accuracy. The cross-activation

efficiency has been found to be considerably greater than that previously reported. It is, however, decidedly smaller than that for collisions between molecules of the same kind.

INTRODUCTION

IN previous communications¹ it was reported that mixtures of gaseous methyl and ethyl ether decomposed at rates determined solely by the partial pressures of the two ethers, and hence the efficiency of energy transfer in cross collisions of the second kind was apparently zero. Kassel² repeated the work and found efficiencies between 66 and 153 percent, depending on the pressure. He therefore concluded that, while the actual values were somewhat uncertain, the cross-activation efficiency must be close to 100 percent.

The present paper describes a repetition of the work with considerably greater accuracy, in an attempt to settle the question of the discrepancy between the two investigations.

SOURCES OF ERROR

Variations in temperature are almost invariably the most important source of error in investigations of the kinetics of homogeneous gas reactions. This is especially true in the case of unimolecular reactions on account of their high temperature coefficients. In the case of the ether decompositions, the rates vary from 10 to 15 percent per degree difference in temperature.

In the previous investigations of Kassel and the writer ordinary electric furnaces were employed. In both cases the average temperature

was probably constant to within about 0.5°C. This, however, is equivalent to about 6 to 7 percent error in the rates of reaction, and will largely mask the effect under investigation. Any attempt to obtain greater accuracy must therefore involve considerably better temperature control.

EXPERIMENTAL PROCEDURE

The reaction velocities were followed in the usual way by admitting the reactant or reactants to a heated silica bulb connected to a capillary manometer, and observing the change in pressure at regular intervals of time. Except for the temperature bath, the apparatus was identical with one which has been used in previous investigations.³ The necessary temperatures were obtained by immersing the reaction bulb in a well-stirred bath of molten lead and tin (80 percent lead).

The bath consisted of a 12 inch length of 7 inch wrought iron pipe, to the bottom of which was welded a flat iron plate. It contained about 4 liters of molten metal. The iron pipe was covered with asbestos paper and wound with 16 gauge nichrome wire. The bath was packed in a steel container with fire-brick and loose asbestos. It was stirred vigorously by a wrought iron stirrer, the shaft of which passed through a small hole in the fire-brick lid.

Temperatures were measured with a chromel-alumel thermocouple in conjunction with a Cambridge thermocouple potentiometer which

¹ Steacie, *J. Am. Chem. Soc.* **54**, 1695 (1932); *J. Phys. Chem.* **36**, 1562 (1932).

² Kassel, *J. Am. Chem. Soc.* **54**, 3641 (1932). I am indebted to Dr. Kassel for communicating his results to me prior to their regular publication.

³ Steacie, *Can. J. Research* **6**, 265 (1932).

could be read to about 0.05°C. The thermocouple was checked at the freezing and boiling points of water, and at the boiling point of sulphur.

Rough temperature control was effected by a 200 cc Pyrex bulb filled with air and immersed in the bath, and connected to a thermal regulator of the ordinary type. With this the temperature could be maintained constant to within about 2°C. During a run the temperature was controlled by hand regulation of rheostats.

On account of the high heat capacity of the contents of the bath, fluctuations in temperature were reduced to a minimum, while the high heat conductivity of the lead-tin mixture and the stirring ensured uniformity of temperature. The temperature could be maintained constant to at least 0.1°C. No variation in temperature throughout the bath could be detected.

The efficiency of the heat insulation is shown by the fact that a temperature of 478°C could be maintained by a power consumption of about 350 watts. On account of the efficient insulation, the bath was almost air-tight, and the lead-tin mixture did not oxidize to any great extent. After about two months continuous operation at 478°C, only about 5 percent of the lead-tin mixture had oxidized.

Methyl and ethyl ether were prepared and stored as previously described.

EXPERIMENTAL RESULTS

The relative rates of reaction were inferred, as in Kassel's investigation, by comparing the fractional pressure increases at 5 minute intervals for 20 minutes in each run. For the first 5 minutes readings were taken at 1 minute intervals and extrapolated to zero time to give the initial pressure. Runs with the separate ethers and with the mixture were made in random order. The values of the fractional pressure increase in 20 minutes for various initial pressures are given in Tables I, II and III.

The data are plotted in Figs. 1, 2 and 3. In order to obtain lines of small curvature, the values of the fractional pressure increase are plotted against $\log_{10} P_0$ rather than against P_0 itself.

It was considered desirable to draw the curves through the experimental points by a compu-

TABLE I. *Fractional pressure increase in 20 minutes for ethyl ether at 478°C.*

| P_0 cm | $\Delta P_{20}/P_0$ | P_0 cm | $\Delta P_{20}/P_0$ |
|-------------|---------------------|-------------|---------------------|
| 35.40 | 0.2720 | 15.89 | 0.2128 |
| 35.34 | 0.2610 | 14.40 | 0.2143 |
| 34.45 | 0.2669 | 14.30 | 0.2080 |
| 33.92 | 0.2642 | 13.27 | 0.1989 |
| 31.49 | 0.2740 | 12.98 | 0.1918 |
| 29.95 | 0.2530 | 12.89 | 0.1850 |
| 28.93 | 0.2535 | 10.91 | 0.1803 |
| 26.65 | 0.2492 | 10.20 | 0.1843 |
| 24.76 | 0.2355 | 9.42 | 0.1632 |
| 23.38 | 0.2578 | 9.23 | 0.1700 |
| 22.90 | 0.2330 | 9.06 | 0.1622 |
| 22.25 | 0.2375 | 8.79 | 0.1801 |
| 20.94 | 0.2238 | 7.58 | 0.1660 |
| 20.53 | 0.2265 | 7.55 | 0.1629 |
| 18.76 | 0.2242 | 7.33 | 0.1498 |
| 18.38 | 0.2233 | 7.19 | 0.1680 |
| 17.74 | 0.2161 | 6.88 | 0.1584 |
| 17.63 | 0.2318 | 6.56 | 0.1645 |
| 17.10 | 0.2122 | 6.50 | 0.1493 |
| 16.42 | 0.2070 | 5.70 | 0.1486 |

TABLE II. *Fractional pressure increase in 20 minutes for methyl ether at 478°C.*

| P_0 cm | $\Delta P_{20}/P_0$ | P_0 cm | $\Delta P_{20}/P_0$ |
|-------------|---------------------|-------------|---------------------|
| 60.23 | 0.3250 | 15.46 | 0.1934 |
| 53.10 | 0.3130 | 14.52 | 0.1665 |
| 52.65 | 0.3120 | 13.68 | 0.1746 |
| 51.80 | 0.2938 | 13.37 | 0.1533 |
| 42.57 | 0.2800 | 11.37 | 0.1530 |
| 35.86 | 0.2510 | 10.89 | 0.1478 |
| 35.50 | 0.2644 | 9.84 | 0.1484 |
| 35.13 | 0.2570 | 9.54 | 0.1440 |
| 34.89 | 0.2455 | 8.86 | 0.1420 |
| 30.35 | 0.2542 | 8.51 | 0.1468 |
| 27.10 | 0.2250 | 7.82 | 0.1176 |
| 24.84 | 0.2136 | 7.48 | 0.1257 |
| 24.73 | 0.2262 | 6.97 | 0.1205 |
| 24.61 | 0.2180 | 6.95 | 0.1180 |
| 22.69 | 0.2019 | 6.74 | 0.1317 |
| 21.74 | 0.2150 | 6.19 | 0.1117 |
| 19.07 | 0.1892 | 6.09 | 0.1132 |
| 17.83 | 0.1926 | 5.41 | 0.1182 |
| 17.53 | 0.1778 | 4.14 | 0.1037 |
| 17.49 | 0.1987 | | |

tational method, so as to avoid any doubts as to the objectivity. The curves have therefore been drawn by fitting the experimental results to empirical equations of the type

$$\Delta P_{20}/P_0 = a + b \log P_0 + c(\log P_0)^2.$$

The fitting has been done by the method of averages, since the additional labor involved in the use of least squares did not seem to be warranted by the experimental accuracy.

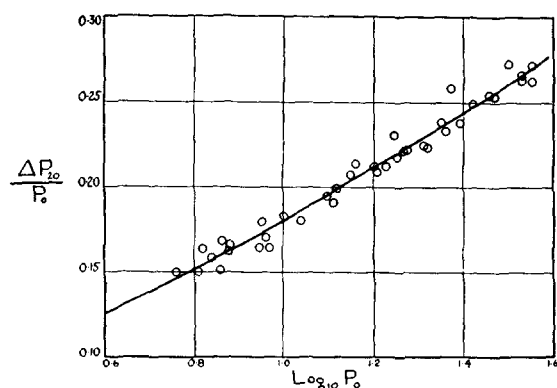


FIG. 1. Ethyl ether.

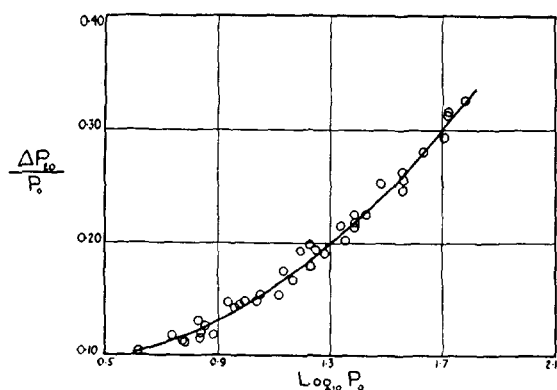


FIG. 2. Methyl ether.

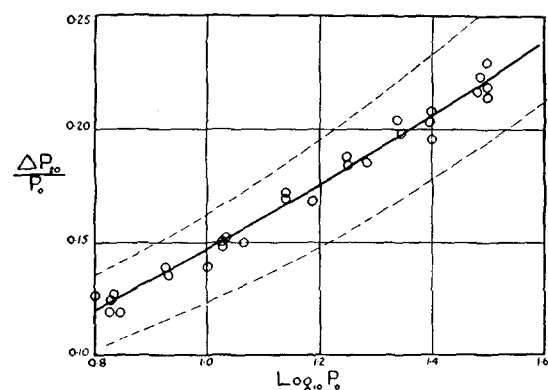


FIG. 3. 1 : 1 mixture.

The cross-activation efficiencies have been calculated by comparing the values of the fractional pressure increase in 20 minutes for the mixture with those calculated for the separate ethers: (A) on the assumption that each ether in the mixture will decompose at a rate determined

TABLE III. Fractional pressure increase in 20 minutes for a one to one mixture of ethyl and methyl ether at 478°C.

| P_0 cm | $\Delta P_{20}/P_0$ | P_0 cm | $\Delta P_{20}/P_0$ |
|-------------|---------------------|-------------|---------------------|
| 31.87 | 0.2298 | 14.95 | 0.1657 |
| 31.78 | 0.2142 | 13.89 | 0.1722 |
| 31.65 | 0.2175 | 13.77 | 0.1700 |
| 31.07 | 0.2238 | 11.72 | 0.1500 |
| 30.48 | 0.2165 | 10.88 | 0.1517 |
| 25.12 | 0.2075 | 10.76 | 0.1525 |
| 24.98 | 0.1950 | 10.72 | 0.1485 |
| 24.87 | 0.2030 | 9.99 | 0.1391 |
| 22.07 | 0.1985 | 8.54 | 0.1356 |
| 21.63 | 0.2047 | 8.41 | 0.1390 |
| 19.51 | 0.1846 | 6.97 | 0.1190 |
| 17.70 | 0.1885 | 6.85 | 0.1284 |
| 17.53 | 0.1824 | 6.73 | 0.1248 |
| 15.61 | 0.1682 | 6.70 | 0.1193 |
| 15.26 | 0.1708 | 6.27 | 0.1275 |

by its *partial* pressure, i.e., on the assumption of zero efficiency of energy transfer between unlike molecules; and (B) assuming that the rate of decomposition of each ether in the mixture will correspond to its rate of decomposition when alone at a pressure equal to the *total* pressure of the mixture, i.e., assuming 100 percent efficiency of energy transfer between unlike molecules. The results are shown in Table IV.

Since complications may arise during the later stages of the reactions, it is obviously desirable to compare the relative rates of reaction at the earliest possible stage. Kassel accomplished this

TABLE IV. Cross-activation efficiencies.

| P_0 cm | $\log_{10} P_0$ | Fractional pressure increase in 20 minutes, observed | | | Fractional pressure increase calculated for mixture, assuming | | Percent cross activation efficiency |
|-------------|-----------------|--|--------------|---------|---|-----------------|-------------------------------------|
| | | Ethyl ether | Methyl ether | Mixture | 100 percent efficiency | Zero efficiency | |
| 4.0 | 0.60 | 0.125 | 0.101 | 0.095 | 0.113 | — | — |
| 5.0 | 0.70 | 0.137 | 0.109 | 0.107 | 0.123 | — | — |
| 6.3 | 0.80 | 0.151 | 0.119 | 0.120 | 0.135 | — | — |
| 7.9 | 0.90 | 0.165 | 0.131 | 0.133 | 0.148 | 0.113 | 57 |
| 10.0 | 1.00 | 0.180 | 0.145 | 0.146 | 0.163 | 0.123 | 58 |
| 12.6 | 1.10 | 0.195 | 0.161 | 0.160 | 0.178 | 0.135 | 58 |
| 15.8 | 1.20 | 0.211 | 0.179 | 0.175 | 0.195 | 0.148 | 57 |
| 20.0 | 1.30 | 0.227 | 0.199 | 0.190 | 0.213 | 0.163 | 54 |
| 25.1 | 1.40 | 0.243 | 0.221 | 0.205 | 0.232 | 0.178 | 50 |
| 31.7 | 1.50 | 0.261 | 0.246 | 0.222 | 0.254 | 0.195 | 46 |
| 39.8 | 1.60 | 0.279 | 0.272 | 0.239 | 0.276 | 0.213 | 43 |
| 50.2 | 1.70 | 0.298 | 0.300 | 0.258 | 0.299 | 0.232 | 40 |
| 63.2 | 1.80 | 0.316 | 0.330 | 0.277 | 0.323 | 0.254 | 39 |
| Mean | | | | | | | 50 |

by determining the fractional pressure increases at 5, 10, 15 and 20 minutes, and extrapolating back to zero time to get the initial rate of reaction. An inspection of Fig. 2 of Kassel's paper, however, shows that there is no uniform trend to the results with increasing increments of time, and within the experimental error virtually the same result is obtained by comparing values of $\Delta P_{20}/P_0$, as by comparing the initial rates.

In the present investigation it was found that efficiencies calculated from a comparison of fractional pressure increases at 5, 10 and 15 minutes showed no significant difference from those tabulated above. No appreciable error is therefore introduced by the use of fractional pressure increases at 20 minutes as a criterion of the relative rates of reaction.

DISCUSSION

As mentioned at the outset, the previous investigation of the writer led to the conclusion that the cross-activation efficiency in mixtures of ethyl and methyl ether was zero, while that of Kassel indicated an efficiency of the order of 66 to 150 percent depending on the pressure. The

present investigation gives values between these, *viz.*, 40 to 60 percent. It is almost certain that the discrepancies between the former investigations were due to temperature variations partially masking the effect under investigation. The values obtained in the present investigation should be considerably more reliable, on account of greatly improved thermostating.

In Fig. 3 the dotted curves indicate the values of $\Delta P_{20}/P_0$ for the mixture of ethers calculated on the basis of zero and 100 percent efficiency of energy transfer between unlike molecules. A comparison of these two curves with the experimental points indicates that a fair amount of reliance may be placed on the numerical values of the cross-activation efficiencies given above.

It may therefore be concluded: (a) that the contention of Kassel is borne out that collisions between unlike complex molecules are definitely effective in producing activation in unimolecular reactions; (b) that there is, however, a definite specificity of energy transfer, collisions between unlike complex molecules being considerably less effective than those between molecules of the same kind.