

imine, that is subsequently converted to lophine, are simultaneously formed. As evidence in favor of this mechanism it has been shown that the degradation of benzalfluorenoneazine yields benzonitrile and 9-imino-fluorene.

A number of other aldazines and ketazines have been pyrolyzed and the decomposition products isolated and identified. In general, when the lophine analog is difficult or impossible to make by the usual method, it is also absent in the pyrolysis of the azine.

Lophine and tetraphenylpyrrole are products of the decomposition of benzyl and dibenzylamine. The pyrolysis in the presence of stilbene leads solely to tetraphenylpyrrole.

High pressures of nitrogen and hydrogen did not appreciably affect the course of the decomposition of benzaldazine.

WASHINGTON, D. C.

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[CONTRIBUTION FROM THE PITTSBURGH EXPERIMENT STATION OF THE U. S. BUREAU OF MINES]

## ENERGY EXCHANGES BETWEEN UNLIKE MOLECULES. THE DECOMPOSITION OF METHYL ETHER, ETHYL ETHER, ACETONE AND THEIR BINARY MIXTURES<sup>1</sup>

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Steacie<sup>3</sup> has recently reported that in mixtures of methyl ether and ethyl ether, each substance decomposes at the rate to be expected from its partial pressure. The decomposition of each of these substances is a homogeneous unimolecular reaction the rate of which, in the usual pressure range, has fallen considerably below the limiting high-pressure value. The conclusion to be drawn from Steacie's report, therefore, is that collisional transfer of energy takes place much more readily when two molecules of ethyl or of methyl ether collide, than when a molecule of ethyl ether collides with one of methyl ether. Such a conclusion is somewhat surprising, since it is a rather more extreme example of specificity than has yet been reported for energy transfers of this character. No directly comparable experiments have been made, but it is known, for example, that ethane is very effective in activating azomethane;<sup>4</sup> the only inert gases which have previously

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<sup>3</sup> Steacie, *THIS JOURNAL*, **54**, 1695 (1932); *J. Phys. Chem.*, **36**, 1652 (1932). I am indebted to Dr Steacie for permitting me to see his complete paper in advance of its publication.

<sup>4</sup> Ramsperger, *J. Phys. Chem.*, **34**, 669 (1930).

been found to be inefficient in transferring energy are such simple ones as helium, nitrogen and carbon dioxide; and in the case of the small reactant molecule nitrous oxide, it is found that activations are produced efficiently by carbon dioxide, and only slightly less so by nitrogen and oxygen. The one striking irregularity in the scheme is furnished by hydrogen, which exhibits remarkably high efficiency in activating a variety of molecules. The case reported by Steacie, then, would be the first in which it had been found that unlike molecules of comparable complexity were not efficient in producing mutual activations. Since there was available here apparatus which could conveniently be used to test this conclusion, the following experiments were made.

### Experimental Method

The reaction vessel was contained in a nichrome-wound furnace which had been designed primarily for work at about 800°; the temperature was controlled automatically by a platinum-platinum-rhodium thermocouple and a Leeds and Northrup controlling potentiometer; there were short period variations of about 2–3°, but throughout the entire work the average temperature was quite constant. There may have been a temperature gradient along the reaction vessel of as much as 5°, but this also did not vary during the work. Hence, it may be supposed that the absolute temperature might be in error by about this amount; actually, the difference in temperature scale from Hinshelwood and Steacie is less than 3°. The temperature used throughout the work, as recorded by the thermocouple, was 487°.

The reaction vessel was a Pyrex flask of about 500 cc. capacity; the attached mercury manometer was of wide bore, and the necessary correction for outside volume was made in the usual way.

C. P. grades of ethyl ether and acetone were used without further purification, except for the pumping out of permanent gases. Methyl ether was made in the apparatus from methyl alcohol and sulfuric acid, separated from methyl alcohol by fractionation, and stored in a cooled trap.

Since these reactions take place in several stages, intermediate products such as aldehydes accumulating in considerable amounts, it seemed desirable to focus attention on the early stages of the reaction; pressure readings were taken at five-minute intervals up to twenty-five minutes, the initial pressure being obtained by a short extrapolation of early, more frequent readings. The manometer was read with an accurate cathetometer, and, except at the very lowest pressures, no appreciable error was possible.

### Results and Calculations

The experimental results for methyl and ethyl ethers and their 1:1 mixture are recorded in Tables I to III in terms of the accumulated fractional

pressure increase,  $\Delta P_t/P_0$ , at five-minute intervals; these have been corrected for the outside volume. It is found that by plotting  $\Delta P_t/P_0$  against

TABLE I  
VALUES OF  $\Delta P_t/P_0$  FOR ETHYL ETHER

Run	$P_0$	$\Delta P_5/P_0$	$\Delta P_{10}/P_0$	$\Delta P_{15}/P_0$	$\Delta P_{20}/P_0$	$\Delta P_{25}/P_0$
25	35.81	0.172	0.332	0.471	0.594	0.716
69	29.38	.145	.296	.427	.558	.674
45	27.55	.124	.272	.429	.562	.677
26	22.54	.137	.291	.425	.540	.646
7	21.53	.146	.293	.423	.534	.642
40	16.98	.107	.209	.324	.422	.533
6	16.89	.106	.235	.371	.488	.588
12	14.45	.079	.176	.286	.404	.508
18	14.20	.097	.206	.319	.428	.520
11	13.59	.113	.216	.310	.406	.515
70	13.50	.092	.187	.281	.377	.487
19	11.44	.097	.190	.278	.362	.454
8	11.03	.090	.201	.313	.409	.489
71	10.30	.093	.187	.269	.368	.450
27	9.31	.080	.163	.251	.342	.439
13	7.31	.078	.156	.228	.302	.363
20	5.72	.064	.136	.220	.297	.365
72	5.58	.054	.118	.178	.256	.324
28	5.00	.074	.140	.199	.270	.335
21	2.83	.058	.121	.168	.227	.282
29	2.65	.063	.113	.155	.213	.281
73	2.59	.044	.083	.113	.157	.196

TABLE II  
VALUES OF  $\Delta P_t/P_0$  FOR METHYL ETHER

Run	$P_0$	$\Delta P_5/P_0$	$\Delta P_{10}/P_0$	$\Delta P_{15}/P_0$	$\Delta P_{20}/P_0$	$\Delta P_{25}/P_0$
62	36.10	0.121	0.276	0.417	0.532	0.628
46	30.09	.093	.210	.345	.477	.590
53	29.60	.117	.245	.380	.514	.627
54	23.19	.096	.218	.346	.458	.552
34	21.70	.113	.242	.376	.506	.616
63	18.77	.067	.148	.231	.314	.402
47	15.02	.076	.162	.249	.330	.409
31	14.44	.094	.188	.276	.354	.429
55	12.00	.065	.138	.222	.301	.378
35	11.06	.079	.162	.248	.342	.431
64	9.78	.042	.095	.169	.241	.317
48	7.51	.033	.068	.110	.161	.219
32	6.95	.066	.127	.193	.259	.318
56	6.27	.036	.077	.118	.161	.198
36	5.29	.042	.082	.124	.166	.215
65	4.72	.031	.059	.097	.139	.179
33	3.61	.031	.065	.105	.157	.194
57	3.18	.035	.056	.084	.105	.136
66	2.71	.021	.041	.065	.090	.106

TABLE III  
VALUES OF  $\Delta P_i/P_0$  FOR METHYL ETHER-ETHYL ETHER MIXTURES

Run	$P_0$	$\Delta P_4/P_0$	$\Delta P_{10}/P_0$	$\Delta P_{14}/P_0$	$\Delta P_{20}/P_0$	$\Delta P_{25}/P_0$
41	32.07	0.113	0.252	0.381	0.493	0.586
49	26.97	.103	.210	.311	.402	.490
37	26.54	.109	.228	.338	.436	.521
42	16.53	.078	.156	.233	.318	.408
58	16.03	.070	.139	.214	.286	.358
50	13.50	.069	.151	.244	.337	.408
38	13.43	.076	.156	.233	.308	.373
59	8.37	.046	.094	.142	.195	.244
43	7.92	.052	.117	.173	.227	.283
39	6.35	.056	.118	.180	.231	.282
51	6.17	.058	.118	.168	.214	.265
44	4.42	.055	.108	.156	.202	.242
60	4.36	.038	.074	.110	.148	.184
52	3.31	.040	.074	.107	.141	.174
61	2.35	.033	.066	.104	.132	.160

$\log P_0$ , lines of only slight curvature are obtained. The experimental results have therefore been smoothed by fitting them to formulas of the type

$$\Delta P_i/P_0 = A + B \log P_0 + C (\log P_0)^2$$

which are, of course, purely empirical. The fitting has been done by least squares, to remove any possible doubt as to its objectivity. Figure 1 shows a typical set of experimental points and the smoothing curve adopted.

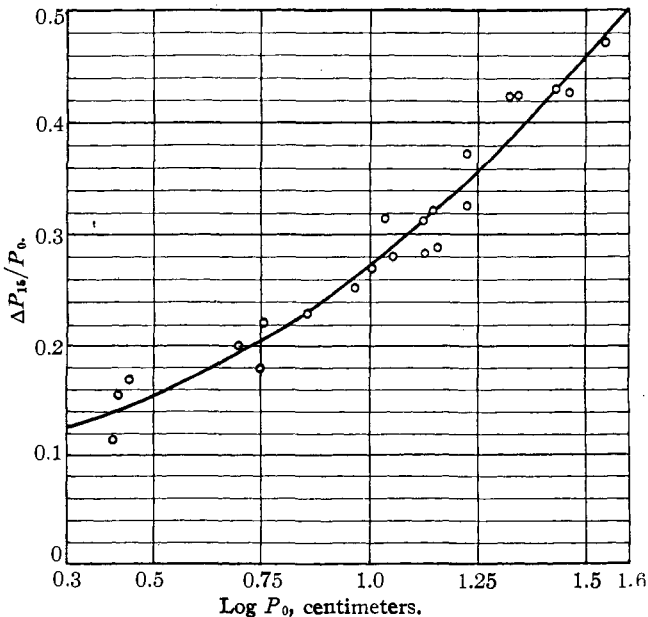


Fig. 1.—Values of  $\Delta P_{14}/P_0$  for ethyl ether.

From the smoothed curves values of  $\Delta P_i/P_0$  at five-minute intervals, for  $\log P_0 = 0.50, 1.00, 1.50$ , for both ethers and the 1:1 mixture were determined; these values are used in constructing Table IV.

TABLE IV  
VALUES OF  $(1/t)(\Delta P_i/P_0)$

		$\Delta P_{25}/25P_0$	$\Delta P_{20}/20P_0$	$\Delta P_{15}/15P_0$	$\Delta P_{10}/10P_0$	$\Delta P_5/5P_0$
At $P_0 = 31.6$ cm.	Methyl ether	0.0248	0.0267	0.0259	0.0248	0.0222
	Ethyl ether	.0284	.0293	.0303	.0313	.0307
	1:1 Mixture	.0224	.0231	.0234	.0236	.0230
At $P_0 = 10.0$ cm.	Methyl ether	0.0136	0.0134	0.0130	0.0125	0.0124
	Ethyl ether	.0178	.0180	.0179	.0175	.0169
	1:1 Mixture	.0125	.0128	.0130	.0128	.0129
At $P_0 = 3.16$ cm.	Methyl ether	0.0053	0.0054	0.0054	0.0050	0.0050
	Ethyl ether	.0108	.0106	.0102	.0110	.0113
	1:1 Mixture	.0074	.0075	.0075	.0078	.0086

It is desirable to determine the initial rate, if possible. This can probably be done best by plotting  $(1/t)(\Delta P_i/P_0)$  against  $t$  and extrapolating

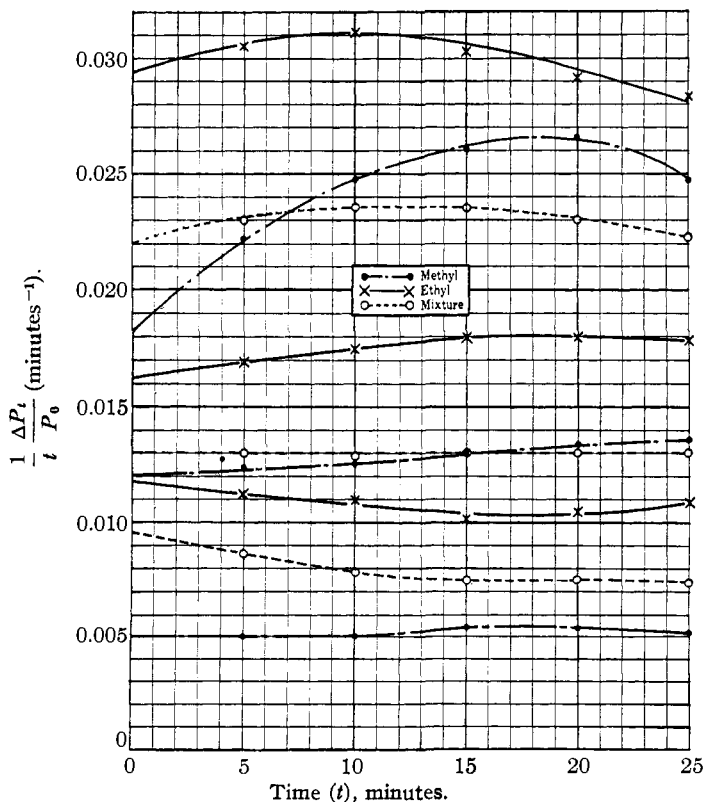


Fig. 2.—Extrapolation to initial rates.

back to  $t = 0$ ; the intercept will be the value of  $k$  for the initial reaction, provided that this reaction results in doubling the pressure and that points have been obtained at values of  $t$  sufficiently small; the latter of these two requirements is the one more likely to be unfulfilled, but without analytical determination of the intermediates, nothing better can be done. Figure 2 shows plots of the kind described, made from the data of Table IV. It is at once apparent that the extrapolated initial rates for the 1:1 mixture are only slightly less than the averages of the rates for the separate ethers at the same pressure. At the higher pressures, as decomposition proceeds, the rate of pressure change for the mixture decreases with respect to that for the separate ethers, but at the lowest pressure this is not the case.

Table V shows the extrapolated initial rates for both ethers and for the 1:1 mixture, and also the rate calculated for the mixture assuming that each ether decomposes at the rate proper to the total pressure; the next column shows the effective pressure of the mixture, assuming that this is the same for both constituents; the final column gives the calculated efficiency of the ethers in cross activation, relative to that in activating themselves. This is calculated as follows. At 10-cm. pressure, for example, the effective pressure of ethyl ether (or methyl) is 8.32 cm., hence 5.00 cm. of methyl ether (or ethyl) is equivalent to 3.32 cm. of ethyl ether (or methyl); this is 66.4% efficient. At the lowest pressure, the errors become rather large, and but little weight is to be given the apparent increase in cross-activation efficiency.

TABLE V  
EXTRAPOLATED VALUES OF  $(1/t)(\Delta P_t/P_0)$

Log $P_0$	Ethyl	$(1/t)(\Delta P_t/P_0)_{t=0}$ , min. <sup>-1</sup>		Mixture	Log $P_{\text{eff}}$	Cross activation efficiency, %
		Methyl	Average			
0.50	0.0118	0.0050	0.0084	0.0094	0.60	153
1.00	.0163	.0120	.0142	.0130	0.92	66
1.50	.0294	.0182	.0238	.0220	1.42	66

This rather elaborate treatment of the data would be unnecessary were it not for the discrepancy between the present results and those of Steacie: the final conclusion does not differ significantly from that reached by casual inspection of plots of direct experimental values of  $\Delta P_t/P_0$  against  $\log P_0$ , which is that the relative efficiency of cross collisions is between 0.4 and 0.70.

A number of experiments were made also with acetone-ethyl ether mixtures, at ratios of 1:1 and 2:1. It does not seem necessary to report these in detail. The acetone decomposes rather more slowly than the ether and presumably at a rate determined solely by its partial pressure; if this is the case, then acetone in acetone-ether mixtures is equivalent to from 80 to 120% of ether.

### Discussion

The disagreement between the results reported by Steacie and those of the present work may easily be traced to the original experimental data.

Table VI gives a comparison of values of  $t_{25}$ , the time for 25% pressure increase, in both cases taken from smoothed curves, and referred to that for ethyl ether as 1.00, to eliminate temperature differences.

TABLE VI

Pressure, cm.	$\frac{t_{25}, \text{methyl}}{t_{25}, \text{ethyl}}$		$\frac{t_{25}, \text{mixture}}{t_{25}, \text{ethyl}}$	
	Steacie	Kassel	Steacie	Kassel
30	1.23	1.27	1.54	1.35
10	1.27	1.34	1.42	1.37

That is, in the present work methyl ether has been found to decompose slightly more slowly, and the 1:1 mixture rather faster than in that of Steacie, the rate for ethyl ether being assumed to be the same. No reason is evident why this should be so. In both investigations the experiments were performed in random order, and hence almost every systematic error was eliminated.

### Summary

It has been found that mixtures of methyl and ethyl ether decompose significantly faster than the rate calculated from the partial pressures of the separate ethers. This result, which is in disagreement with a report made by Steacie, means that the transfer of internal energy between unlike ether molecules at collisions takes place about as readily as between like ether molecules; the exact value found is 66%, on which, however, not much confidence should be placed. A similar result is found for mixtures of acetone and ethyl ether.

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### NOTE

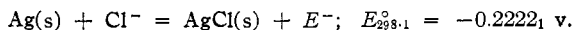
#### The Standard Electrode Potentials of Silver-Silver Chloride and Calomel Electrodes and the Single Potentials of Calomel Electrodes

BY HUGH M. SPENCER

Carmody's<sup>1</sup> accurate data on the potentials of the cells  $H_2$ ,  $HCl$  ( $xM$ ),  $AgCl(s)$ ,  $Ag$  in quartz apparatus, when transformed into the form

$$\log \gamma + \text{const.} = \frac{E^\circ}{0.11831} + \log \gamma = -\frac{E}{0.11831} - \log m_{\pm}$$

superimpose beautifully on the curve of  $\log \gamma$  vs.  $m^{1/2}$ , calculated by Randall and Young.<sup>2</sup> The constant obtained in this way is  $-1.8782$ , corresponding to



whereas Carmody's extrapolation of  $E'$  yielded  $-0.2223$  v.

<sup>1</sup> W. R. Carmody, *THIS JOURNAL*, **54**, 188 (1932).

<sup>2</sup> M. Randall and L. F. Young, *ibid.*, **50**, 989 (1928).