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owing to the calibration on which it is based, but for computing transference numbers at infinite dilution it is justifiable to use it provided the corresponding limiting ionic mobility for sodium ion (50.10) is employed. It was previously shown,[1] however, that MacInnes and Shedlovsky's data could be represented more closely by the equation $\Lambda_0'=90.94+101._1C$ than by the equation they employ $\Lambda_0'=90.97+90C$; here Λ_0' is the Onsager function $(\Lambda+2\beta\sqrt{C})/(1-\alpha\sqrt{C})$ where Λ is the equivalent conductivity at concentration C. Even better agreement with the experimental data is obtained if the extended Onsager-Shedlovsky equation[6] is employed

$$\Lambda_0'=90.94+152._1C+20._7C\log C. \qquad (1)$$

TABLE II.

C	0	0.01	0.02	0.05	0.10	0.15
t_+	0.5509	0.5540	0.5553	0.5575	0.5598	0.5606

In any event, the conductance data correspond more nearly to $\Lambda_0=90.94$ than to $\Lambda_0=90.97$, i.e., $t_+{}^0$ for sodium acetate should be 0.5509, in exact agreement with the result obtained from the mean plot of Fig. 1. Table II gives values of t_+ for a few round values of the concentration; the entries are on the average about 0.0003 greater than those given by Longsworth[2] in his Table VI; this is within his estimated probable error for that table.

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[6] L. Onsager and R. Fuoss, J. Phys. Chem. **36**, 2689 (1932); T. Shedlovsky and A. S. Brown, J. Am. Chem. Soc. **56**, 1066 (1934); T. Shedlovsky, A. S. Brown and D. A. MacInnes, Trans. Electrochem. Soc. **66**, 165 (1934); A. R. Gordon, J. Chem. Phys. **7**, April (1939). If δ indicates the difference $\Lambda_{\text{calc}}-\Lambda_{\text{obs}}$, the closer agreement of Eq. (1) above with the experimental data, as compared with MacInnes and Shedlovsky's Eq. (5) is evident from the following table. The comparison is for the fourteen solutions listed in their Table I.

	$\Sigma\delta^2$	$\Sigma\delta$	$\Sigma\lvert\delta\rvert$	Max. $\lvert\delta\rvert$
MacInnes and Shedlovsky, Eq. (5)	2.88	0.14	0.48	0.11
This paper, Eq. (1)	1.90	0.00	0.38	0.07

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By means of an optical lever manometer the decomposition velocities of methylene diacetate, ethylidene diacetate and paracetaldehyde have been measured down to pressures of 0.05 mm of mercury. No falling off in reaction rate has been observed. The minimum numbers of internal degrees of freedom contributing to the activation energies are thus 16, 18 and 64, respectively.

INTRODUCTION

IT has been shown[1] that ethylidene diacetate, paracetaldehyde and their homologs decompose in the vapor state by a homogeneous first-order mechanism. The apparatus employed did not permit satisfactory rate measurements to be made at initial pressures lower than several centimeters of mercury. The present paper deals with measurements at initial pressures between 0.05 and 3 millimeters.

EXPERIMENTAL

The pressure change at constant volume was followed with an optical lever manometer resembling that of Shrader and Ryder,[2] mounted in a heavy iron frame resting on large rubber stoppers on the concrete basement floor. A small glass bulb attached to a lever arm and mirror and carried by a fine torsion wire floated on the mercury in one arm of the manometer. The torsion wire was stretched across the prongs of a spring brass fork inserted and adjusted from

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[1] C. C. Coffin *et al.*, Can. J. Research **5**, 636 (1931); **6**, 417 (1932); **7**, 75 (1932); **9**, 603 (1933); **11**, 180 (1934); **15**, 229 (1937); **15**, 247 (1937); **15**, 254 (1937); **15**, 260 (1937). Trans. Roy. Soc. Can. **27**, 161 (1933).

[2] J. E. Shrader and H. M. Ryder, Phys. Rev. **13**, 321 (1919).

Table I. *Summary of reaction velocity data.*

Run No.	Initial P	T° Abs.	$k\times10^4$	$-\log k$	$1/T\times10^3$
Methylene Diacetate					
25	0.90 mm	590.6	16.8	2.665	1.696
26	.36	589.2	22.5		
27	.14	589.2	21.9		
28	.20	589.2	20.6		
29	.40	589.3	26.0		
1	.29	585.1	18.5	2.708	1.709
2	.26	585.1	20.1		
3	.22	585.2	19.4		
4	.23	585.1	21.0		
5	.37	585.0	18.5		
6	.34	585.0	20.4		
7	.32	577.0	11.7	2.932	1.733
8	.22	577.0	11.7		
9	.30	577.0	13.2		
10	.39	577.1	9.3		
11	.26	577.2	12.4		
12	.32	569.8	8.29	3.137	1.755
13	.52	569.7	7.39		
14	.41	569.4	7.15		
15	.14	569.7	7.53		
16	.36	569.8	6.96		
17	.39	569.7	6.45		
18	.35	552.6	2.15	3.516	1.810
19	.38	551.9	2.82		
20	.30	552.2	2.96		
21	.35	552.6	3.15		
22	.26	552.7	3.45		
23	.36	552.6	3.36		
24	.33	552.6	3.45		
Ethylidene Diacetate					
1	.49 mm	570.1	6.97	2.121	1.755
2	.60	570.1	7.68		
3	.40	570.1	7.30		
4	.40	570.1	8.20		
5	.74	566.5	7.65		
6	.52	558.6	3.00	2.495	1.790
7	.35	558.6	3.40		
8	.37	551.6	2.78	2.551	1.807
9	.60	554.8	2.83		
10	.57	554.8	3.37		
11	.52	550.3	2.35		
12	.36	552.7	2.74		
13	.22	537.1	1.60	2.910	1.858
14	.25	537.1	1.60		
15	.80	538.4	1.00		
16	.44	538.4	1.09		
17	.68	538.4	1.00		
18	.62	538.4	1.22		
19	.30	538.4	1.11		
20	.18	531.1	7.42	3.015	1.881
21	.59	532.6	7.61		
22	.34	533.5	10.09		
23	.46	530.2	11.50		
24	.50	534.4	7.61		
25	.42	530.2	12.80		
26	.35	530.1	10.70		
27	.40	530.1	11.30		
28	.55	533.6	7.91		
29	0.72 mm	519.8	2.02	3.556	1.923
30	.43	519.8	3.15		
31	.66	519.8	2.82		
32	.73	519.9	2.82		
33	.55	519.9	2.83		
34	.58	519.0	2.54		
35	.52	520.0	3.32		
36	.29	509.1	2.86	3.634	1.962
37	.34	509.3	2.03		
38	.42	509.4	2.42		
39	.34	509.6	1.97		
Paracetaldehyde					
1	.90 mm	566.4	112	1.932	1.765
2	1.19	566.3	112		
3	1.99	566.0	109		
4	1.03	566.7	118		
25	.27	566.1	120		
26	.27	567.2	129		
27	.20	583.4	402	1.388	1.713
28	1.10	584.2	403		
29	.40	583.6	404		
30	.20	585.4	428		
31	.27	583.6	406		
32	.05	573.1	182	1.735	1.742
33	.39	573.2	179		
34	.40	574.2	188		
35	.22	574.0	178		
36	.23	573.8	188		
37	.15	574.4	199		
38	.14	572.9	177		
39	.11	575.2	177		
40	.10	572.8	183		
41	.25	574.0	176		
42	.25	574.0	168		
43	.90	573.2	161		
5	.79	554.7	48.0	2.296	1.802
6	1.76	554.7	52.6		
7	1.17	556.6	54.9		
8	1.21	553.8	48.3		
9	1.16	554.0	49.6		
10	3.28	554.7	52.0		
11	.99	554.7	49.0		
12	.74	544.3	21.0	2.674	1.838
13	.67	544.2	21.8		
14	.88	543.6	20.9		
15	.50	541.8	20.0	2.740	1.851
16	.55	540.1	18.6		
17	.99	538.4	15.0		
18	1.65	524.2	5.68	3.263	1.904
19	1.50	524.2	5.55		
20	.80	525.1	5.53		
21	1.05	525.7	5.41		
22	1.03	524.3	4.99		
23	.87	524.8	5.18		
24	.85	525.9	5.91		

above through a ground glass and Picein joint. The two sides of the manometer, a short U-tube of 6-cm Pyrex, were connected by a stopcock. The spot of light from the mirror was brought through the wall of the manometer tube and focused on a vertical ground glass scale. Three different combinations of lenses, floats and lever arms were used magnifying the mercury movement 50, 91 and 250 times. Actual pressures were obtained by frequent calibration over the whole range against an oil manometer.

The reaction chamber was an 1 l. Pyrex flask sealed inside a 2 l. flask in such a way that it could be heated by the vapor of mercury boiling under a definite pressure. It was connected by stopcocks with pumps and reactant reservoir. To smooth out vibrations from the bumping mercury in the boiler the manometer and reaction chamber were connected through a 5-turn 8-cm spiral of very thin-walled 4-mm tubing. The dead space due to the manometer and connecting tubing was less than 3 percent of the total volume and is not taken into account in the following calculations.

Several different samples of each reactant were studied. They were purified as already described.[1]

RESULTS

The results obtained are summarized in Table I. In all cases readings were taken at equal time intervals and velocity constants calculated by the method of Guggenheim.[3]

In Fig. 1, $-\log k$ is plotted against $1/T$. The straight lines of the figure are those given by the previously published rate equations.[1] It is evident that no falling off in rate occurs in this pressure range. The fact that the methylene diacetate points are appreciably above the line is probably due to the increased importance of the heterogeneous reaction[4] at the lower pressures. A steady drift in the final pressure always occurred in the runs with this ester.

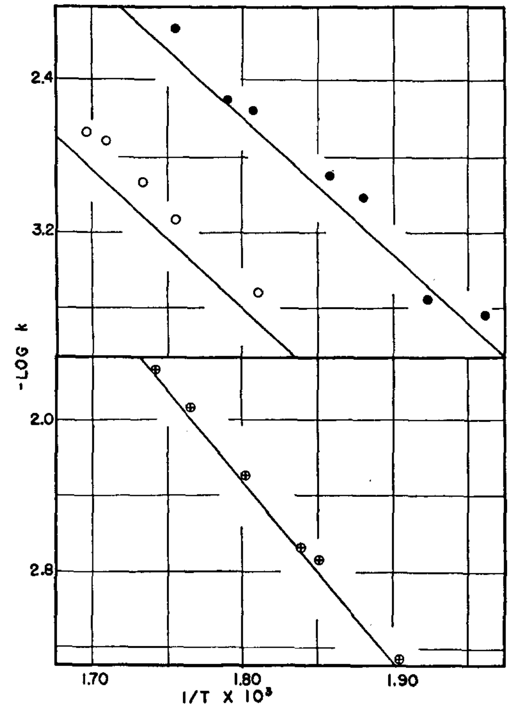

FIG. 1. Reaction rates at low pressures. ●, methylene diacetate; ○, ethylidene diacetate; ⊕, paracetaldehyde.

Following the treatment of Hinshelwood[5] the minimum number of contributing squared terms is found to be about 16, 18 and 64 for methylene diacetate, ethylidene diacetate and paraldehyde, respectively. Molecular diameters are taken as 4×10^{-8} cm.

Since this work was done Burnett and Bell have published data on paraldehyde that checks with the above results.[6]

A Bursary from the National Research Council of Canada is acknowledged by one of us (J. R. D.).

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[3] E. A. Guggenheim, Phil. Mag. **2**, 543 (1926).

[4] C. C. Coffin and W. B. Beazley, Can. J. Research **15**, 233 (1937).

[5] C. N. Hinshelwood, *Kinetics of Chemical Change* (Oxford University Press, 1933).

[6] R. le G. Burnett and R. P. Bell, Trans. Faraday Soc. **34**, 420 (1938).