8. *The Kinetics of the Depolymerisation of Bimolecular Nitroso*iso*propylacetone.*

By KENNETH D. ANDERSON and DALZIEL LL. HAMMICK.

BAMBERGER (*Ber.*, 1903, **36**, 685) observed that when a colourless solution of bimolecular nitroso-*tert.*-butane in benzene was exposed for a short time to sunlight, it remained colourless, whereas a portion of the same solution kept for the same time in the dark depolymerised to the deep blue unimolecular form. On warming, or standing in the dark, the colourless solution that had been illuminated also became blue. From these observations, Bamberger concluded that the depolymerisation of the bimolecular nitroso-molecules was arrested by light (" Sonnenlicht hemmt die Depolymerisation der Doppelmolekel "). Bimolecular nitroso*iso*propylacetone, $[CMe_2(NO){\cdot}CH_2{\cdot}CO{\cdot}CH_3]_2$, was found to behave in a similar manner.

These phenomena appeared sufficiently remarkable to warrant a more detailed investigation, and an account is now given of the kinetics of the thermal (dark) depolymerisation of the second compound, which was chosen in preference to the first because of its greater accessibility. A photochemical study of the substance is not yet complete, but sufficient progress has been made to enable us to state that Bamberger's hypothesis of a polymerisation process catalysed by light is erroneous. Longer exposure of the colourless solutions to light completely destroys the solute, and the explanation of his observations is simply that under suitable conditions the rate of photodecomposition of the blue unimolecular form is greater than its rate of production from the colourless double molecules. A short illumination does not destroy all the nitroso-compound present, and hence blue single molecules are re-formed on warming or standing in the dark.

EXPERIMENTAL.

The rate at which colourless bimolecular nitroso*iso*propylacetone depolymerises in the dark in benzene solution was followed by observing the rate of increase in density of colour due to the production of the blue unimolecular form. This was done by means of a Hilger–Nutting spectrophotometer, in which the absorption tube was mounted in a small brass cylindrical jacket. Water from an electrically controlled thermostat was circulated rapidly through the jacket, and the temperature of the absorption tube maintained constant (thermometer in the jacket) to ± 0·05°. The whole apparatus was set up in a dark room, and the solutions were illuminated only during the actual process of determining their absorptions.

Before the optical method could be used to study the kinetics of the depolymerisation, it was necessary to determine the absorption spectrum of the blue unimolecular form for visible light, and also to connect the absorption for the wave-length selected for use in the kinetic measurements with the concentration of the coloured solute. It was possible to obtain this essential preliminary information owing to the fact that depolymerisation of the bimolecular nitroso-compound is complete after a few hours' standing in the dark (Bamberger, *loc. cit.*).

Preparation of Materials.—Nitroso*iso*propylacetone, m. p. 75·5°, was prepared according to the method of Bamberger (*loc. cit.*). The solvent was A.R. benzene frozen out three times and distilled from phosphoric oxide in a current of dry air.

*The Absorption Spectrum of Nitroso*iso*propylacetone.*—The data in Table I were obtained for solutions in benzene; under D is given the colour density for light of wave-length λ transmitted by a solution of concentration 0·036 g.-mol./l. in a tube of length 1·95 cm.

TABLE I.

λ, Å.	*D.*	λ, Å.	*D.*	λ, Å.	*D.*	λ, Å.	*D.*	λ, Å.	*D.*	λ, Å.	*D.*
7440	0·222	6950	1·050	6700	1·523	6450	1·280	6000	0·641	5500	0·202
7300	0·312	6900	1·196	6650	1·514	6400	1·194	5900	0·554	5400	0·160
7200	0·445	6850	1·332	6600	1·504	6300	1·016	5800	0·452		
7100	0·650	6800	1·425	6550	1·442	6200	0·908	5700	0·378		
7000	0·900	6750	1·488	6500	1·371	6100	0·763	5600	0·284		

It will be seen that maximum absorption occurs at about λ 6700. This line was therefore used in all subsequent experiments.

The Variation of Absorption with Concentration.—The following data were obtained using this line and the same tube, concentrations (C) being given in g.-mol./l.

C	0·0263	0·0374	0·0506	0·0583
D	1·106	1·558	2·152	2·454

The relation between C and D is linear, and is given by $D = 42{\cdot}1 \times C$.

Velocity Measurements.—Rates of depolymerisation were determined in benzene solution at seven temperatures between 8·09° and 21·86°. Solutions were made up rapidly in solvent maintained at the temperature selected for experiment, and introduced into the jacketed absorption tube ($l = 1{\cdot}95$ cm.). After a short period to allow thermal equilibrium to be reached, the colour density D was found by means of the spectrophotometer and redetermined after successive intervals of time. Preliminary experiments with pure solvent gave the correction for the absorption due to the benzene, and a short extrapolation of the graph of D against time to zero absorption enabled zero time to be fixed. By means of the relation $D = 42{\cdot}1 \times C$, where C is the concentration of the unimolecular form, the amount of depolymerisation was obtained. The results, which show that at each temperature the rate of depolymerisation follows a unimolecular law of constant k, are given below; C_0 is the initial concentration of bimolecular form (g.-mol./l.), and t is given in minutes.

Experiments 1 *and* 2 : at 8·09°, with initial concentrations $C_0' = 0{\cdot}0264M$ and $C_0'' = 0{\cdot}0346M$; t' and t'' are the respective times for successive fractional changes.

Change, %	10	20	30	40	50	60	70
t'	24	50	82·5	115	154	200	263
t''	23	51	81	113	150	193	250
t (mean)	23·5	50·5	81·8	114	152	196·5	256·8
$k \times 10^3$	4·47	4·41	4·36	4·58	4·56	4·88	4·69

Change, %.	Expt. 3. $T = 12{\cdot}1°$. $C_0 = 0{\cdot}0282$.		Expt. 4. $T = 13{\cdot}35°$. $C_0 = 0{\cdot}0287$.		Expt. 5. $T = 14{\cdot}72°$. $C_0 = 0{\cdot}0292$.		Expt. 6. $T = 16{\cdot}0°$. $C_0 = 0{\cdot}0299$.		Expt. 7. $T = 20{\cdot}5°$. $C_0 = 0{\cdot}0294$.		Expt. 8. $T = 21{\cdot}85°$. $C_0 = 0{\cdot}0242$.	
	t.	$k \times 10^3$.	*t.*	$k \times 10^3$.	*t.*	$k \times 10^3$.	*t.*	$k \times 10^3$.	*t.*	$k \times 10^3$.	*t.*	$k \times 10^3$.
10	12	8·76	11·5	9·15	8·5	12·37	7·5	14·02	4	26·30	3	35·08
20	27	8·25	24	9·30	18	12·38	16	13·93	8	27·89	7	31·88
30	44·5	8·01	38	9·40	27	12·17	25·5	13·98	12	29·76	10·5	34·02
40	63	8·30	53	9·64	42	12·16	36	14·16	18	28·38	15	34·06
50	84	8·24	71	9·99	56·5	12·26	48	14·42	24	28·88	20·5	33·81
60	109	8·41	97·5	9·40	75	12·14	63	14·53	32	28·63	27·5	33·32
70	142	8·47	129	9·33	98·5	12·21	84	14·32	42	28·67	36	33·45

In Table II are given the data necessary for the derivation of the heat of activation of the process of depolymerisation. The values for the viscosity of benzene are taken from the International Critical Tables.

TABLE II.

T.	$10^3/T_{\text{abs.}}$	$k \times 10^3$.	log 10^3k.	$\eta \times 10^3$.	log k/η.
8·09°	3·558	4·54	0·6571	7·825	$\bar{1}$·7635
12·1	3·508	8·35	0·9217	7·330	0·0560
13·35	3·492	9·46	0·9750	7·175	0·1192
14·72	3·474	12·23	1·0875	7·035	0·2402
16·00	3·460	14·19	1·1519	6·900	0·3131
20·50	3·407	28·35	1·4526	6·425	0·6448
21·85	3·391	33·58	1·5260	6·320	0·7253

Interpretation of Results.—The graph of log ($10^3 \times k$) against $1/T_{\text{abs.}}$ is a straight line, the slope of which yields a value $E = 24{,}030$ cals. for the Arrhenius heat of activation. The plot of k/η against $1/T_{\text{abs.}}$ is also a straight line, and from its slope we find $E' = 26{,}600$ cals. This will be the true heat of activation on the assumption that each collision between a solvent and a solute molecule with energy equal to E' results in depolymerisation, for then the unimolecular velocity constant will be given by $k = Z \,.\, e^{-E'/RT}$, in which $Z = 3\pi\eta\sigma/2m$, the number of solvent–solute collisions per second (Moelwyn-Hughes, "Kinetics of Reactions in Solution," p. 159). On introduction of the values for the viscosity of benzene at 20°, $\eta = 6{\cdot}47 \times 10^{-3}$, for the molecular diameter, $\sigma = 8 \times 10^{-8}$ cm., and for $m = (C_6H_{11}O_2N)_2 = 258$, Z is found to be $5{\cdot}7 \times 10^{12}$, and $e^{-E'/RT} = 1{\cdot}82 \times 10^{-20}$ very nearly. These data lead to a value for k at 20° of $10{\cdot}4 \times 10^{-8}$, which is less than the observed value (27×10^{-3}, by interpolation) by a factor of about 10^{-5}. This discrepancy disappears if the energy of activation is regarded as being distributed between a number of internal degrees of freedom of the reacting molecule. Using Hinshelwood's expression (Moelwyn-Hughes, *op. cit.*, p. 163), we find F, which is one less than the number of degrees of freedom involved, to be 4 [since $(E'/RT)^4/\underline{|4} = 1{\cdot}77 \times 10^{-5}$]. Introducing also the correction for the persistence of velocities (*idem, ibid.*, p. 28), we obtain a calculated value for k at 20° of 24×10^{-3}, as against the observed value of 27×10^{-3}.

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THE DYSON PERRINS LABORATORY, OXFORD.

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