potential (ΔV) may rise considerably less rapidly than the surface density of the film (13% less rapidly in the case of certain polymers of ω-hydroxydecanoic acid). This is usually attributed to the mutual effect of the surrounding dipoles. However, it is quite probable that in the case of the *d*-pimaric acid, the conspicuous *decrease* in the surface potential with increased surface density is due to a changing orientation of the individual molecules in such manner as to further the opposition or compensation of the intramolecular dipoles.

Additional studies relating potential variations to temperature changes are now in progress.

VI. Summary

1. Surface potential and force–area relations for monomolecular films of a saturated and unsaturated pimaric acid were studied. The corresponding curves are shown.

2. An improved procedure for obtaining more accurate clean-surface potentials is described.

3. The maximum thickness of the mono-layer is about 12 Å. for both compounds. The coefficients of compressibility are calculated.

4. The structures of the pimaric acids are compared with that of cholesterol, and their orientations in surface films are related to the different positions in which the polar groups are located. The experimental data compare favorably with the results to be expected from model measurements.

5. The surface potential of the tetrahydro-*d*-pimaric acid is about 200 mv., whereas that of the unsaturated compound is about 100 mv. An unprecedented decrease in the surface potential on compression was observed in the case of the unsaturated acid films. It is considered probable that these facts may be related to an increasing intramolecular dipole compensation on compression.

CHICAGO, ILLINOIS RECEIVED AUGUST 22, 1935

[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA]

Heterogeneous Reaction Kinetics. The Effect of Light Exposure on the Kinetics of Thermal Decomposition of Silver Oxalate

BY ARTHUR F. BENTON AND GEORGE L. CUNNINGHAM

In reactions of the type $A(s) = B(s) + C(g)$, which are normally autocatalytic in nature, existing evidence shows that the rate depends on two separate factors, formation of nuclei of product and subsequent growth of these reaction centers. However, a satisfactory quantitative treatment of the kinetics has not yet been attained. With this objective in view we have studied, both experimentally and theoretically, the rate of decomposition of a light-sensitive solid on which nuclei have previously been produced by controlled irradiation.

Silver oxalate was chosen as a suitable material, since it decomposes at convenient temperatures and apparently yields only silver and carbon dioxide, uncomplicated by side reactions. MacDonald and Hinshelwood[1] found the reaction to be autocatalytic, and the rate sensitive to adsorbed ions and to oxygen. Sheppard and Vanselow[2] showed that sulfur compounds greatly accelerate the reaction. Arens and Eggert[3] found that silver oxalate–gelatine plates were made developable by exposure, and resembled silver chloride emulsions both in sensitivity and spectral range.

Experimental Methods

Approximately 1-g. samples of silver oxalate were decomposed in the dark in Pyrex bulbs heated by suitable vapor baths provided with electric heating and regulated pressure. The evolved gas was continuously removed by means of a Sprengel pump and fed into the lower end of a water-jacketed, mercury-filled buret, where its volume was measured at regular intervals. Absence of leaks in the all-glass apparatus was assured by overnight test before each experiment.

In the later experiments (Oxalate II), samples were illuminated when desired with light from a 1000-watt tungsten-filament lamp provided with a reflector. The light, after traversing in order a lens system, 6 cm. of running water, a suitable color filter and a shutter, was reflected downward to the bulb by a metallic mirror. The filter was Corning G586AW, which transmits from about 320 to 400 mμ, with a maximum at 370 mμ. All exposures were made with the oxalate at room temperature. The

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(1) MacDonald and Hinshelwood, *J. Chem. Soc.*, **127**, 2764 (1925); see also Hoitsema, *Z. physik. Chem.*, **21**, 137 (1896).

(2) Sheppard and Vanselow, THIS JOURNAL, **52**, 3468 (1930).

(3) Arens and Eggert, *Phot. Korr.*, **67**, Congress No., 17 (1931).

sample was contained in a cylindrical bulb 4 cm. in diameter, closed at the top by fusing to a plane disk of Pyrex glass. At its lower end the bulb was drawn down to a funnel shape, terminating in a 2-mm. capillary, through which air or other gas was drawn in, to stir the sample during exposure. This procedure occasioned only a negligible loss of sample, *e. g.*, 1.7% in eight hours.

The light absorbed by the oxalate was measured by surrounding the reaction bulb with a 2-mm. layer of a 1% solution of *o*-nitrobenzaldehyde in purified acetone. Based on the measurements of Hyman, quoted by Weigert and Brodman,[4] this arrangement absorbed 99.6% of λ 366, and thus substantially all the light in our experiments, centering at 370 mμ. The light absorbed by the solution, at least between λ 366 and λ 436, produces 0.5 molecule of *o*-nitrosobenzoic acid per quantum.[5] The acid was determined by conductance measurements, with known mixtures of aldehyde and acid containing a constant total amount (1%) of the two isomers as standards. For stirred samples 40 to 50% of the incident light was absorbed.

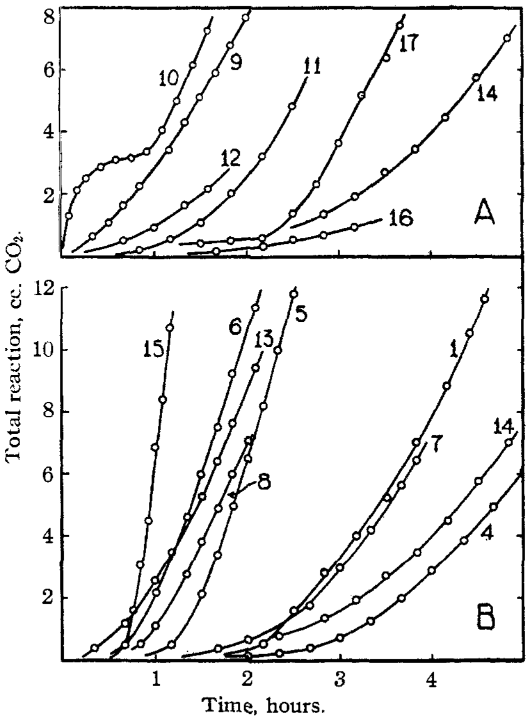

Fig. 1.—Decomposition of oxalate I: effect of various factors (Table I).

Materials.—The first batch of silver oxalate (Runs 1–17) was prepared by continuously adding, during seventy-five minutes, a solution of 25 g. of C. P. silver nitrate in one liter of distilled water to a solution containing 20 g. of C. P. sodium oxalate dissolved in 3 liters of water, with vigorous mechanical stirring. After ten thorough washings the precipitate was dried in a vacuum desiccator over sulfuric acid. Exactly the same procedure was followed for the second batch. The oxalate was prepared and stored in a dark room, only a minimum of red light being used when necessary.

Experimental Results

In the data given below, the course of reaction is expressed as total cc. of carbon dioxide evolved by the whole weight of sample as a function of time. The gas volumes represent an average temperature of 26° and an average pressure of 750 mm. (at 0°). Since we were primarily interested in the earlier stages, the reaction was usually followed only to 5–10% of completion, except at higher temperatures.

Silver Oxalate I.—The experiments with this preparation were designed to show the influence of various factors on the course of decomposition. All except Run 15 were made at 100 ± 0.2°. The results are shown in Fig. 1 (A and B), and the necessary data in Table I. All exposures were made with a 100-watt tungsten filament lamp at a distance of 20 cm. The numbers listed in Column 4 of Table I give the disposition of the samples during exposure: (1) spread out in thin layer in air, (2) stirred magnetically in vacuum, (3) stirred in water, then dried in air. Color filters were used only in Run 11 (Wratten 16, passing λλ > 520 mμ) and Run 12 Wratten 47A, passing λλ 360–520).

TABLE I

DATA FOR FIGURE 1

Run	Sample, g.	Hr.	Exposure Method
4	0.88	0	..
7	.86	0	..
14[a]	1.52	0	..
15[b]	0.89	0	..
1[c]	1.28	0	..
5	0.86	1	(1)
8	.80	3	(1)
6	.93	18	(1)
13	1.42	3	(2)
16[d]	1.4	0	..
17[e]	1.48	0	..
9	0.80	3	(3)
10	.97	54	(3)
11	.78	3	(3)
12	1.34	3	(3)

[a] Sample dried ten months in vacuum. [b] Decomposed at 118.5°. [c] Decomposed in carbon dioxide at 1 atm. [d] Sample mixed with residue from Run 15 in stream of carbon dioxide. [e] Sample ground in agate mortar.

These experiments show that the decomposition was not markedly affected by long drying of the

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(4) Weigert and Brodman, *Trans. Faraday Soc.*, **21**, 453 (1925–6). Slightly higher values were obtained by Weigert and Prückner, *Z. physik. Chem.*, Bodenstein Festband, 775 (1931).

(5) Weigert and Brodman, *ibid.*, **120**, 24 (1926); Leighton and Lucy, *J. Chem. Phys.*, **2**, 756 (1934).

oxalate, by the presence of carbon dioxide, or by contact of the sample with *foreign* particles of silver. The rate was somewhat increased by fine grinding. Previous exposure to light greatly increased the rate, the effect being relatively greater for shorter exposures. Wave lengths longer than 520 mμ were surprisingly effective, but the effect per quantum was undoubtedly much greater for shorter wave lengths.

After the last point shown for Run 7, a twelve-hour exposure at room temperature produced 0.06 cc. of gas. That light alone could effect decomposition was also indicated by the discoloration from exposure in Run 10. On carrying Run 8 to completion the evolved gas was 99.6% of theoretical; not more than 0.04% was unabsorbed by potassium hydroxide.

Silver Oxalate II.—With this material all exposures were conducted as described under "Methods." The results of a series of runs at 100°, with different stirring gases during exposure, are shown in Fig. 2A, and the pertinent data in Table II. It may be observed that the unexposed sample (19) decomposed much more slowly than Oxalate I, in spite of the identical method of preparation. Another run (18) under the same conditions gave results practically identical with 19. Contact with air (Run 22) retarded the initial decomposition, doubtless due to the strong chemosorption of oxygen by silver,[6] but this effect was later overcome. During the exposure in Run 26 the sample evolved 0.05 cc. of gas, or 0.12 molecule per quantum absorbed.

TABLE II

RUNS AT 100° FOLLOWING EXPOSURE IN DIFFERENT GASES

Run	Wt., g.	Gas	Exposure, hr.	Quanta absorbed $\times 10^{-18}$
19	1.42	None	0	0
20	0.91	CO_2	8	7.1
21	1.02	N_2	8	8.7
22	1.09	Air	8	5.5
26	1.42	None	20	11.9

Figure 2B shows the results obtained at 100° with samples previously exposed for varying times, all being stirred with air. Table III gives the necessary data. It is evident that while these early stages of the reaction are more rapid with increasing exposure, the effect is relatively much less for the longer exposures.

A series of runs at 118°, following varying exposure with air stirring, is detailed in Table IV and in Fig. 3, where *rate* is plotted against time. At this temperature exposure evidently has relatively little effect, but the actual increase in total reaction at any time, as compared with unexposed samples, is much greater than at 100°.

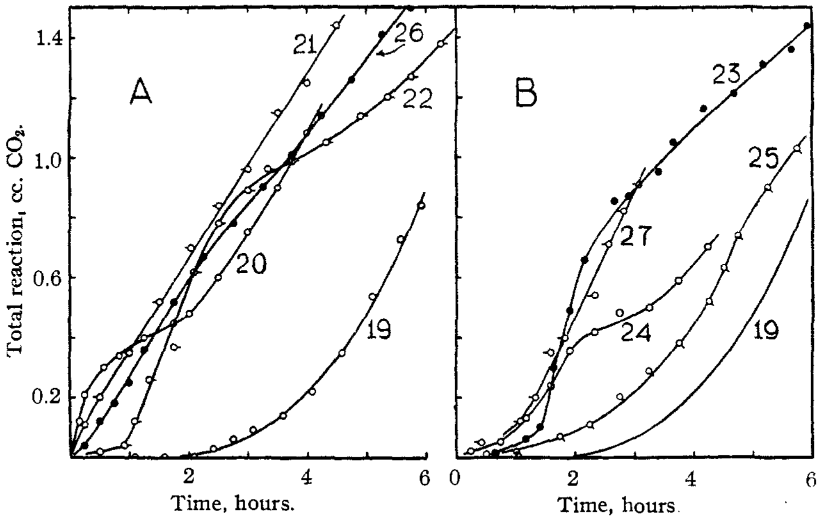

Fig. 2.—Decomposition of oxalate II at 100°: A, effect of gas used for stirring during exposure (Table II): B, effect of exposure time (Table III).

TABLE III

RUNS AT 100° WITH VARYING EXPOSURE

Run	Wt., g.	Exposure, hr.	Quanta absorbed $\times 10^{-18}$
19	1.42	0	0
25	0.96	$^1/_3$	0.37[a]
24	1.56	1	1.2
27	1.02	4	4.4[a]
22	1.09	8	5.5
23	1.19	20	22.2

[a] Calculated on basis of Run 23.

TABLE IV

RUNS AT 118° WITH VARYING EXPOSURE

Run	Wt., g.	Exposure, hr.	Quanta absorbed $\times 10^{-18}$
34	0.90	0	0
36	1.11	1	0.5[a]
35	1.06	8	3.7
44[b]	1.18	0	0

[a] Calculated on basis of Run 35. [b] 117°.

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[6] Benton and Drake, THIS JOURNAL, **56**, 255 (1934); Drake and Benton, *ibid.*, **56**, 506 (1934).

In Run 44 the unexposed sample was subjected to occasional rapid changes in temperature between 117 and 100°. Comparison of the average of the rates at 117° before and after each temperature change with the intervening rate at 100° gives ratios of 5.1, 3.9 and 4.5, or an average of 4.5. The general effect of a wider range of temperature on unexposed samples is shown in Fig. 4, to which the following data apply.

Run	19	42	34	37	30
Wt., g.	1.42	1.38	0.90	0.92	1.30
Temp., °C.	99.9	109.8	118	131	138

At the upper limit of the curves shown for Runs 30 and 37 the samples exploded.

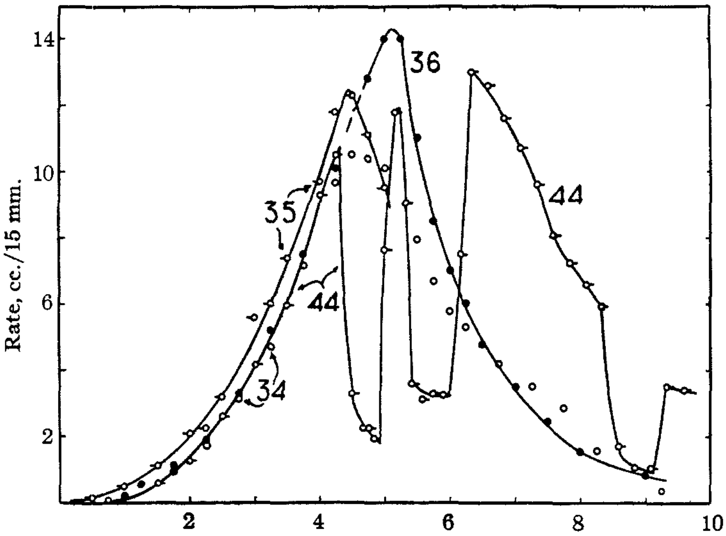

Fig. 3.—Rate of decomposition of oxalate II at 118° (Table IV).

At 80° a 1.53-g. sample gave no measurable evolution of gas in thirteen and one-half hours. Another sample (1.20 g.) gave no gas in seven hours at 80°; on changing the bath temperature to 100°, the course of reaction was practically identical with that in Run 19 where the sample had not been preheated. Hence the rate of formation of nuclei at 80° must be inappreciable. A third sample (1.15 g.) was exposed to room light for thirty minutes and then heated for two and three-tenths hours at 80°, during which time not more than 0.01 cc. of gas was evolved. When the temperature was raised to 100° decomposition began at once in the normal manner for exposed samples. After 0.6 cc. had been given off, the temperature was brought back to 80°, where in two and one-half hours only 0.02 cc. was evolved. Thus the rate of growth of nuclei at 80° is extremely small, but appreciable.

A single granule of Oxalate II, weighing perhaps 1 mg., was decomposed at 118° in a tiny bulb protected from light (Run 45). The evolved gas was measured by the depression of the mercury level in an adjoining 1-mm. capillary, the pressure being maintained at 1 mm. When readings (cm.) on the capillary are plotted against time, the curve is almost identical with that shown in Fig. 4 for Run 42.

Silver Oxalate III.—This material was prepared in exactly the same manner as I and II except that, instead of a slight excess of sodium oxalate, a 100% excess of silver nitrate was used. In a run at 100° an unexposed sample (1.27 g.) gave yields only about half as great as Oxalate II (Run 19). Another sample (1.11 g.), exposed for one hour exactly as in Run 24, gave rates at 100° practically identical with the latter. Although it is possible that adsorbed silver nitrate retards the reaction, the much greater difference in activity between Oxalate I and II, which were prepared alike, renders this conclusion doubtful.

Theoretical Results

The following considerations are based on the assumption that the formation of nuclei and their subsequent growth are essentially independent processes. Without sharply defining the size of a "nucleus," we may let the number of them which have formed up to time t equal n. Let the volume of the solid which has reacted around a particular nucleus be $x = f(t - \tau)$, where τ is the time at which the nucleus came into existence, and f is some function. Then at any time the number dn of nuclei which appeared in the interval $d\tau$ will have spread through a volume $x dn$, and the total volume decomposed at time t will be

$$V = \int_{\tau=0}^{\tau=t} x dn \qquad (1)$$

To integrate this expression it is necessary to make assumptions regarding the variation of x and n with time.

Solutions of the problem for certain special cases have already been given. Thus Topley and Hume[7] assumed that reaction in each particle spread from a single nucleus, and that all particles were nucleated simultaneously at zero time. Bradley, Colvin and Hume,[8] assuming nucleation according to a probability law, treated the case in which the reaction, once started on a particular granule, spreads instantaneously over its whole surface. In each case the relations obtained were successful in reproducing the later stages in the decomposition of certain salt hydrates, but failed to account adequately for the earlier stages. It is our belief that the early stages of interfacial reactions are particularly amenable to a general treatment, such as that which follows.

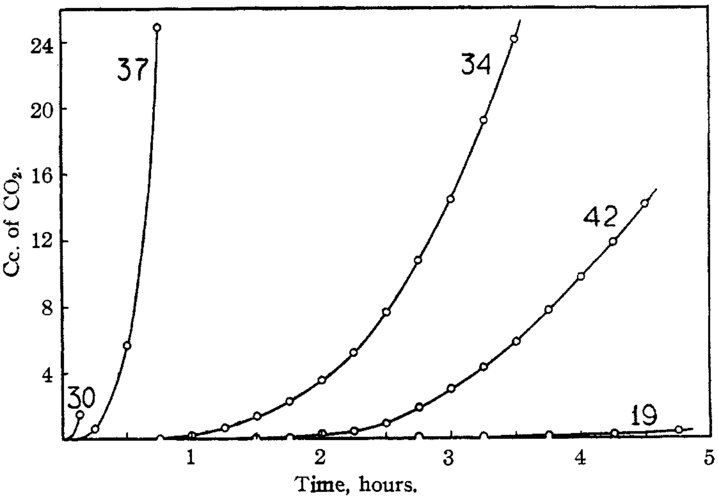

Fig. 4.—Decomposition of oxalate II (unexposed) at different temperatures.

In single crystals decomposition, once started, has been found to progress in directions parallel to prominent lattice planes,[9] and with a *constant* velocity characteristic of each direction.[10] The porous, disperse product remaining usually retains the gross size and shape of the original material, and exerts no retarding effect on the rate. Let u be the *mean* linear velocity of advance of the interface. Then the volume decomposed at any time becomes $u^3(t - \tau)^3$ if the nucleus appeared at a corner, twice this if the start occurred on an edge, and four times if it began on a face. If reaction is assumed to spread out with a spherical front, these values must be multiplied by $\pi/6$. In general we may write for the volume decomposed

$$x = Bu^3(t - \tau)^3 \qquad (2)$$

Since most workers have observed that nucleation occurs preferentially at corners, B will doubtless be near unity. Even for a typical microcrystalline material, complicated by intergrowths and other irregularities, Eq. 2 might be expected to hold for a given granule until the reaction zones spreading from two or more neighboring nuclei begin to overlap.

The problem of the rate of formation of nuclei is less clear. An obvious assumption is that $\mathrm{d}n = k(N - n)\mathrm{d}\tau$, where n is the number formed up to time τ, and N is the total number of potential nuclei in the whole sample (possibly "active spots"), all assumed equally active. This expression leads to $\mathrm{d}n = k(N - n_0)e^{-k\tau}\mathrm{d}\tau$, where n_0 is the number of nuclei, if any, present at the start.

With these values inserted in Eq. 1 the total volume decomposed at time t becomes

$$V = \int_{\tau=0}^{\tau=t} Bu^3(t - \tau)^3 k(N - n_0)e^{-k\tau}\mathrm{d}\tau$$
$$= k(N - n_0)Bu^3\,[6e^{-kt}/k^4 + (t^3/k)(1 - 3/kt + 6/k^2t^2 - 6/k^3t^3)]$$

If the exponential term is now expanded as a power series in t, all terms below t^4 cancel, and

$$V = (k/4)(N - n_0)Bu^3t^4(1 - kt/5 + k^2t^2/5\cdot 6 - \cdots)$$

But this does not include the reaction due to growth of the n_i nuclei, such as those produced by irradiation, which were present at zero time. Including these, and multiplying by the ratio r of measured product (in our case cc. of carbon dioxide) to the volume of solid reactant, we have for the total yield

$$Y = r[(k/4)(N - n_0)Bu^3t^4(1 - kt/5 + \cdots) + n_iBu^3t^3 - v_0n_i] \qquad (3)$$

n_i and n_0 will be equal provided photochemical and thermal nucleation involve the same "active spots." The last term, representing the purely photochemical yield in the production of the n_i nuclei, each of volume v_0, may be neglected. Unless the rate of nucleation k is very great, the higher terms in the parentheses are also small; thus when $n = N/3$, $kt/5$ is only 0.08. Hence, as a fair approximation for the earlier stages, the yield for unexposed samples (n_i and $n_0 = 0$) should vary nearly as t^4, with a smaller average

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(7) Topley and Hume, *Proc. Roy. Soc.* (London), **A120**, 211 (1928).

(8) Bradley, Colvin and Hume, *ibid.*, **A137**, 531 (1932); *Phil. Mag.*, [7] **14**, 1102 (1932).

(9) Kohlschütter, *Kolloid Z.*, **42**, 254 (1927).

(10) Hume and Colvin, *Proc. Roy. Soc.* (London), **A125**, 635 (1929).

power of t for exposed samples. These relations will of course fail to hold after the time when the first granules nucleated have been completely decomposed.

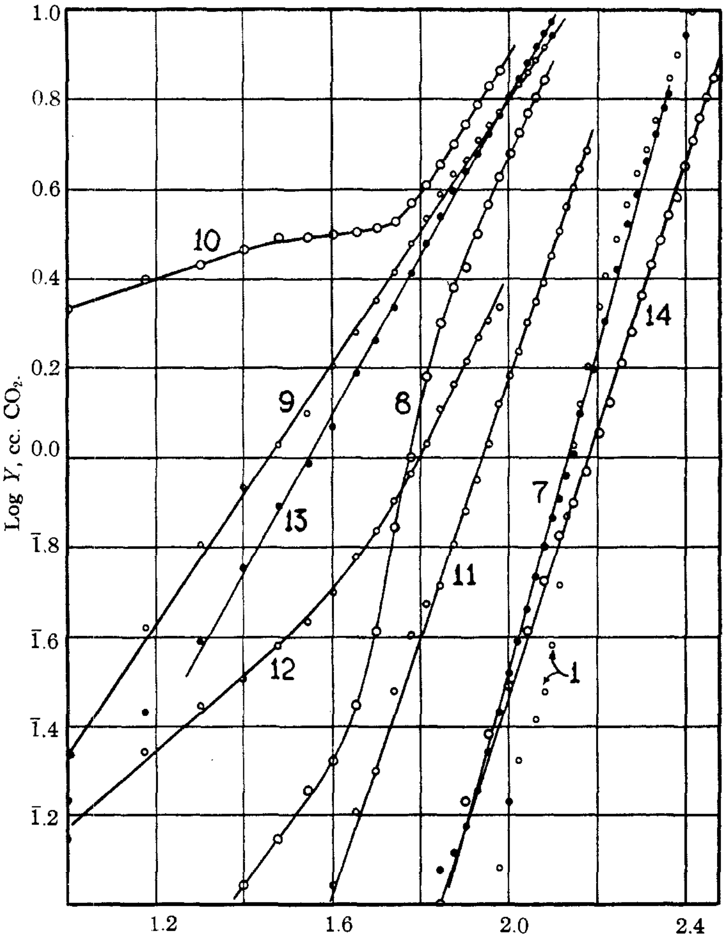


Fig. 5.—Log-log plot for decomposition of oxalate I at 100°.

TABLE V

OBSERVED AND CALCULATED YIELDS IN RUN 44

$Y = 1.176 \times 10^{-7} t^{3.60}$

Time, min.	Y, obsd., cc.	Y, calcd., cc.
60	0.21	0.30
75	.69	.66
90	1.29	1.28
105	2.24	2.22
120	3.52	3.59
135	5.47	5.49
150	8.07	8.03
165	11.4	11.3
180	15.6	15.5
195	20.5	20.6
210	26.4	26.9
225	34.3	34.6
240	43.6	43.6
255	54.1	54.2

It has been assumed that the reaction, even though its early rate may be very small, actually begins at zero time, in other words there is no "incubation" period. This is the case for silver oxalate decomposition and nearly all other interfacial decompositions. The mechanism of nucleation here assumed cannot be applied to cases, such as many reduction reactions, where a real incubation period occurs.

Discussion

The above development suggests that plots of log Y *versus* log t should give nearly straight lines for the earlier stages of decomposition. (Complete decomposition of a 1-g. sample is equivalent to Y = 160 cc.) Such plots for representative runs are shown in Figs. 5 and 6. In the majority of cases the curves closely approximate straight lines. Prolonged exposure tends to make the early yield relatively too large. In a few cases the curves are S-shaped, particularly in Run 8 (also 5 and 6) where the sample was exposed in air without stirring. The gaps in Curves 14 and 19 represent overnight interruptions with the sample at room temperature. Table V indicates the extraordinary fidelity with which the results for an unexposed sample (44) may be repro-

TABLE VI

CONSTANTS IN THE EQUATION $Y = at^m$

Run	m	$-\log a$
	Oxalate I, 100°	
7	3.6	7.6
14	3.1	6.7
11	2.9	5.7
12	1.9	3.5
13	1.7	2.7
9	1.4	2.1
10	1.6	2.3
	Oxalate II, 100°	
19	3.5	9.1
	Oxalate II, 118°	
34	3.4	6.5
44	3.6	6.9
36	3.2	6.0
35	2.9	5.2
45	3.9	(13.3)

duced by the simple expression $Y = at^m$. The last observed value represents 28% of the total reaction.

In Table VI are recorded the values of m and a (cc. at 26°, 750 mm.) in the equation $Y = at^m$, for all runs in which this relation was followed over a major part of the observed data.

Runs are listed downward in order of increasing exposure to the active wave lengths. In general, the requirements of Eq. 3 are qualitatively fulfilled, that is, m decreases and a increases with increasing exposure. It is noteworthy that for unexposed samples, m is close to 3.5, for both batches and for different temperatures, whereas the corresponding values of a differ widely. The difference from the theoretical value of $m = 4$ might be ascribed to a fraction of the crystals having one very small dimension, or to a variation among the N "active spots" in ability to form nuclei. The most probable explanation, however, is to be found in a continuing exhaustion of those granules which happened to be nucleated early, any sharp change in rate being obscured because of variation in particle size.

Likewise, for exposed samples, Eq. 3 calls for $m = 3$ near the start of reaction, whereas slopes only half of this value were occasionally found. It is proper to note here, however, that slopes much below 3 were found only when the exposed sample had been in contact with air before decomposition (Runs 12, 9, 10) or when, as in Run 13, the illumination was nonuniform due to inadequate stirring.

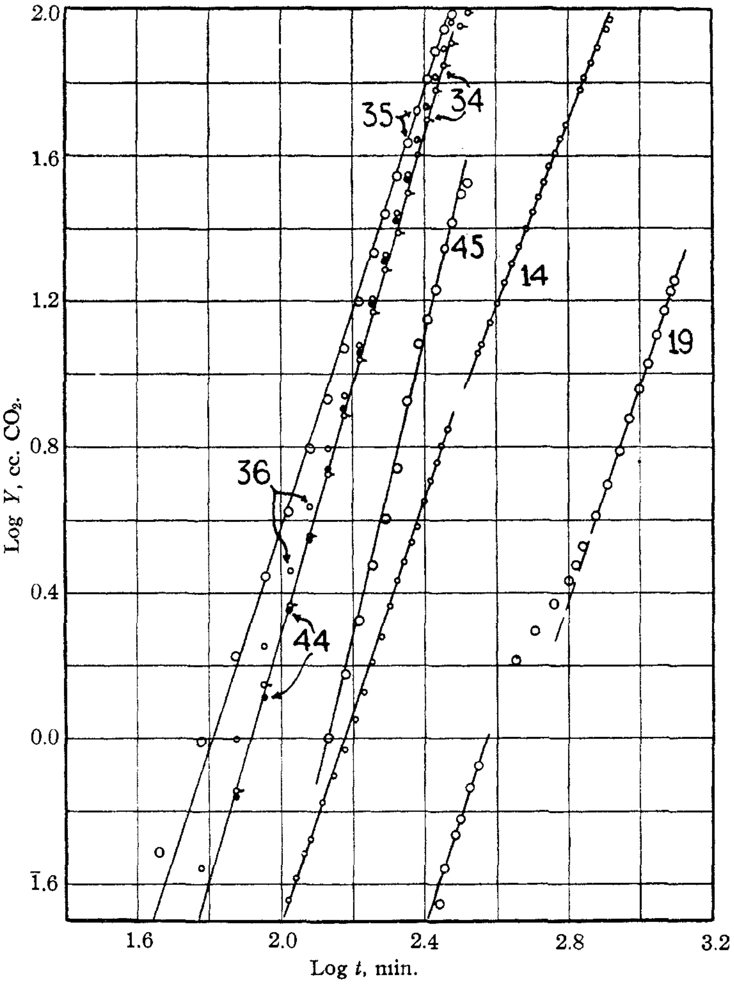


Fig. 6.—Log-log plot for decomposition of oxalate II.

In cases of short exposure (n_i and $n_0 \ll N$) the yield from thermally produced nuclei will be the same with or without exposure, so that ΔY, the increase due to exposure, should be proportional to the n_i photonuclei. This relation is roughly valid for exposures up to one hour (Fig. 2B). The increasing importance of n_0 may explain the relatively smaller effect of longer exposures, or it may be that the number of photonuclei increases less rapidly than the number of quanta absorbed.

For a given (short) exposure and time the values of ΔY at two temperatures should be proportional to the corresponding values of u^3. For Oxalate II a quantum absorption of 0.5×10^{18} produced at t = two hours a ΔY of about 0.15 cc. at 100° (based on Runs 24 and 25), and 0.77 cc. at 118° (Run 36). Hence u^3 increased by a factor of 5.1 and u by a factor of 1.7, corresponding to an activation energy E_u of 8600 cal. An independent value of E_u may be obtained from the relative rates at 117 and 100° in Run 44 (Fig. 3)—a procedure which is justified because at 100°, as Run 19 shows, new nuclei make no appreciable contribution to Y for at least two hours. Over the 17° interval in Run 44 u increased by a factor of $\sqrt[3]{4.5} = 1.65$, equivalent to $E_u = 8500$ cal., in agreement with the former value.

For the early stages of reaction with unexposed samples the relative yields at a given time should vary as kNu^3, and the yields per gram of sample as ku^3. For Runs 34 and 19 the relative yields per gram at twenty-five-minute intervals from $t = 195$ to $t = 300$ min. were 300, 280, 290, 290, 260. Hence, in this 18.5° interval ku^3 increased by a factor of 290, so that k increased by a factor of $290/5 = 58$, equivalent to an activation energy E_k of 64,000 cal. for the nucleation process. The conclusion that the temperature coefficient of nucleation is much greater than that of growth of nuclei is confirmed by the qualitative experiments at 80°.

An E_k of 64,000 cal. is equivalent to an einstein of λ 445 mμ. With Oxalate I wave lengths > 520 mμ caused nucleation, but the much greater rates of decomposition of this material suggest that its E_k may have been less than 64,000.

Summary

In the decomposition of solid silver oxalate variations in rate due to long drying, preparation with excess of one or the other reagent, or fine grinding, were scarcely greater than the differences between two samples prepared and treated alike. Exposure to light, particularly to $\lambda\lambda < 520$ mμ, greatly increased the rate of the subsequent thermal reaction. Contact with oxygen during exposure resulted in a marked initial poisoning as compared with exposure in nitrogen, carbon dioxide or vacuum. The increase in yield at any time over that for unexposed samples was roughly proportional, for the shorter exposures, to the number of quanta absorbed, but relatively much less for longer exposures. The effect of exposure was relatively less at higher decomposition temperatures. In the exposure itself λ 370 mμ produced about 0.1 molecule of carbon dioxide per quantum absorbed.

The earlier stages of decomposition have been found to be in fair agreement with a quantitative formulation of the kinetics (Eq. 3), based on simple assumptions regarding the formation of nuclei of product and their subsequent growth. In agreement with the theory, the extent of reaction at any time t, in the earlier stages, is approximately proportional to t^m, where m is found to be 3.5 for unexposed samples, but progressively less for increasing exposure.

For a particular sample of oxalate the activation energy of nucleation is about 64 kcal., while that for growth of nuclei is 8.5 kcal.

UNIVERSITY, VA. RECEIVED JUNE 3, 1935

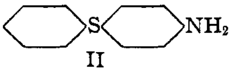
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

The Molecular Rearrangement of Sulfanilides. II

BY MAURICE L. MOORE[1] AND TREAT B. JOHNSON

In a previous paper[2] on this subject we have discussed the rearrangement of certain aromatic sulfanilide compounds of type I. We have shown

I



II

that on heating these alone or in the presence of an excess of the corresponding amine they undergo rearrangement to the corresponding aromatic para-amino sulfides II. In this paper we shall describe a second type of rearrangement characteristic of sulfanilides which is brought about by the action of alcoholic sodium hydroxide solution.

Smiles and his co-workers,[3] who have recently investigated the chemical behavior of *o*-amino sulfones and sulfides, have made the interesting observations that certain representatives of both series undergo molecular rearrangement in alkaline media to form the corresponding sulfinic acid and mercaptan derivatives of diphenylamine, respectively. The same type of rearrangement was also found to take place with the *o*-hydroxy sulfones.[4] The amino sulfide compound shows an irregularity in chemical behavior as is illustrated by the following observation. It was found that the acetyl and the 2-nitrobenzoyl derivatives of 2-nitro-2′-aminodiphenyl sulfide, for example, would undergo rearrangement to the corresponding diphenylamine structures, whereas under the same conditions the parent amine itself, the picryl and the benzenesulfonyl deriva-

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[1] A. Homer Smith Research Fellow in Organic Chemistry, 1934–1935.

[2] THIS JOURNAL, 57, 1517 (1935); see also *Science*, 81, 643 (1935).

[3] (a) Warren and Smiles, *J. Chem. Soc.*, 914 (1931); 2774 (1932); (b) Evans and Smiles, *ibid.*, 181 (1935); (c) Wight and Smiles, *ibid.*, 340 (1935).

[4] (a) Warren and Smiles, *ibid.*, 1040 (1932), (b) Levi and Smiles, *ibid.*, 1488 (1932); (c) Kent and Smiles, *ibid.*, 422 (1934).