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THE OXIDATION OF BENZOYL-ORTHO-TOLUIDINE AT A BENZENE-WATER INTERFACE WITH SPECIAL REFERENCE TO THE TEMPERATURE COEFFICIENT OF THE REACTION RATE

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In a recent paper, R. P. Bell² has reported some reaction rate measurements for the system aqueous potassium permanganate-benzoyl-*o*-toluidine dissolved in benzene. Oxidation occurs at the interface and the solubility relations at 25°, according to Bell, are such that an appreciable amount of homogeneous oxidation of *A*³ cannot occur. Bell finds that the rate of this reaction is independent of the rate of stirring of the benzene layer over a four-fold range, and that the 10° temperature coefficient for the range 15–25° is 13, corresponding to an energy of activation of 43,700 cal. He finds that the reaction is of the first order with respect to the permanganate, and that the rate increases with the concentration of *A* for low concentrations, but becomes independent of concentration at about 5–6 grams/liter. This suggests the formation of a saturated film at this concentration, and since the same conclusion is reached from an application of the Gibbs-Helmholtz equation to the interfacial tensions for the system water-benzene-*A*, this conclusion is probably correct. The permanganate is almost certainly negatively adsorbed and the reaction may well occur upon the impact of permanganate ions on the adsorbed film of *A*. It is this mechanism which Bell has proposed.

Our attention was directed to this work by the extremely large temperature coefficient which Bell found. Few reactions have temperature coefficients greater than 4, and none, so far as we are aware, in excess of 7, at temperatures where their rates are appreciable. No mechanism which we could construct was capable of accounting for the magnitude of the observed rate; the discrepancy in all cases amounted to a factor of at least

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² Bell, *J. Phys. Chem.*, **32**, 882 (1928).

³ Hereafter, for brevity, benzoyl-*o*-toluidine will be designated by *A*, and benzoyl anthranilic acid, one of the oxidation products, by *B*.

10^{20} . It thus seemed that, if this value 43,700 calories was in any way related to an actual energy associated with the reaction, some new ideas would have to be introduced into reaction rate theory to account for the speed of this reaction. Before this was attempted, however, it appeared desirable to verify the experimental results, and this we have attempted to do. Our work disagrees with that of Bell in three particulars.

1. Bell gives a list of desirable characteristics for an interfacial reaction, to which the one selected presumably conforms. One of these characteristics is that no solid should separate out. He states especially that although *B* is rather insoluble in benzene and but slightly soluble in water, his rates apply to the initial part of each run, during which it all remained in solution. He makes no statement about manganese dioxide, but by implication one would suppose that it is not formed. Since the reaction is started in a neutral solution and since this solution can scarcely avoid becoming alkaline as the reaction proceeds,⁴ the formation and precipitation of manganese dioxide is to be expected. It actually occurred in all of our experiments, and we cannot see how it could have been absent in Bell's.⁵

2. Bell varied the rate of stirring of the benzene layer by a factor of 4, keeping the rate of stirring in the water layer constant, and found no change in the rate. He therefore concluded that the rate of reaction was independent of the rate of stirring. We found that when the rate of stirring in both layers was increased, the rate of reaction increased markedly.

3. We did not verify Bell's value of 13 for the temperature coefficient, but instead found a value of about 2.

Experimental Part

A was prepared by benzoylation of technical *o*-toluidine in benzene solution. The resulting material was filtered hot and *A* separated out upon cooling. It was then recrystallized from benzene. Three separate preparations were used during the work. The first (Sample I) was not washed with hydrochloric acid at any stage. Sample II was washed with dilute hydrochloric acid and then with water after recrystallization and Sample III with the same reagents before recrystallization. Samples I and II melted at 139–140° and Sample III at 142°. The value given by "International Critical Tables" is 143°.

The reaction was carried out in a five-liter bottle of brown glass. The area of the

⁴ The equation $2\text{KMnO}_4 + A \longrightarrow 2\text{MnO}_2 + B + 2\text{KOH}$ certainly would lead to increased alkalinity. So would $6\text{KMnO}_4 + 5A + 4\text{H}_2\text{O} \longrightarrow 6\text{Mn}(\text{OH})_2 + 5B + 6\text{KOH}$. Any further reaction which took place could only increase the alkalinity.

⁵ Since the submission of this paper, we have been informed by Bell (private communication) that in the initial parts of his runs the manganese dioxide did not separate out, but that on standing this did take place. It appears that it is formed as a colloid. Our own observations on this point are incomplete, since we could not examine the surface closely until after the reaction was stopped, but we have some reason to believe that in our experiments also the initial stage does not involve precipitation, though the colloid does not appear to have been as stable as in Bell's experiments.

interface was 220 cm.². A single stirrer was used for both solutions, with three paddles in the water layer and one in the benzene. A protecting tube of about 5 cm. length surrounded the portion of the stirrer which passed through the interface, so that the disturbance produced would be confined to a small region, but the alignment was good enough so that even that small part of the interface was not noticeably agitated. The paddles were perfectly straight horizontal rods, about 8 mm. in diameter and 20 mm. long. The three paddles in the water layer were mounted at angular intervals of 120° and vertical intervals of 10 mm. The chief reason for the rather inefficient design was that otherwise it would have been almost impossible to give even a crude idea of the amount of stirring produced.

The course of the reaction was followed by withdrawing 10-cc. samples of the permanganate solution from time to time and titrating with freshly prepared ferrous ammonium sulfate solution; this seemed preferable to the oxalic acid which Bell used, since it was unnecessary to heat the solution during the titration and the chance of reaction between *B* and the permanganate in the hot acid solution was thus avoided. The pipet with which the solution was withdrawn passed through a protecting tube which contained no benzene layer; since almost all of the manganese dioxide collected at the interface, this made the sampling more reliable than it would have been otherwise.

The thermostatic regulation was entirely adequate. Fluctuations as great as 0.05° did not occur.

Altogether 20 runs were made. The first five were preliminary and since they were made with a different stirrer or in a different reaction vessel than the others the results will not be reported. Run 6 was made with 1400 cc. of benzene solution, containing 5.36 grams/liter of *A*, and 1750 cc. of about 0.035 *N* permanganate. All of the following runs were made with 1000 cc. of benzene containing 6 g. of *A*, and 1750 cc. of about 0.005 *N* permanganate. Runs 6-10 were made at 25.0° using Sample I. In each of these runs one or more changes was made in the rate of stirring during the run, and with a single exception each change resulted in a perfectly definite change in the rate of reaction. The exception was in run 9, which showed no abrupt change when the rate of stirring was increased from about 20 r.p.m. to 80; the measurements were not continued a sufficiently great time after the change to make the results definite and the run could never be duplicated. In general it may be said that at rates of stirring of 80 or more the results are reproducible with quite fair accuracy, but that at lower rates they are erratic. For example, in run 4, with a different stirrer, no reaction was observed in five hours at 20 r.p.m., nor in one hour at 33, but a rapid reaction set in at 160; in run 9, as has been said, a slow reaction occurred at 20 r.p.m.; in run 10 no reaction had occurred after eight hours at speeds of 10-45 r.p.m.; run 11, with Sample II, gave reaction at 20-50 r.p.m., while run 12, with the same sample but at 27.9°, showed no reaction in three hours at 20-40 r.p.m. Since the time available for these experiments was limited, we were forced to abandon this part of the investigation without reaching a definite conclusion as to the relation between the rate of reaction and the rate of stirring at rates less than 50 r.p.m. Between 50 and 250 r.p.m., however, there is a very definite and marked dependence on the rate of stirring. This is shown by Fig. 1, in which the observed rates in runs 6, 7, 9 and 10 (run 8 gave about 100 times the normal rate, but it also showed dependence on the stirring) are plotted against the rate of stirring. The rates are given in moles of permanganate per hour per cm.² of surface per unit molarity. The general trend of the points is quite obvious except at low rates. The rather considerable scattering is attributable mainly to two causes; it was not always possible to keep the rate of stirring quite constant, and some of the abscissas represent mean values which may not be accurate. Most of the points at higher rates were obtained from the later parts of runs, when varying amounts of man-

ganese dioxide were present; this, or some other reaction product, appears to have a poisoning effect on the surface, so that rates which were not obtained under exactly corresponding conditions should not be expected to agree perfectly. The best evidence that between 50 and 250 r.p.m. the rate does depend on the stirring is obtained from

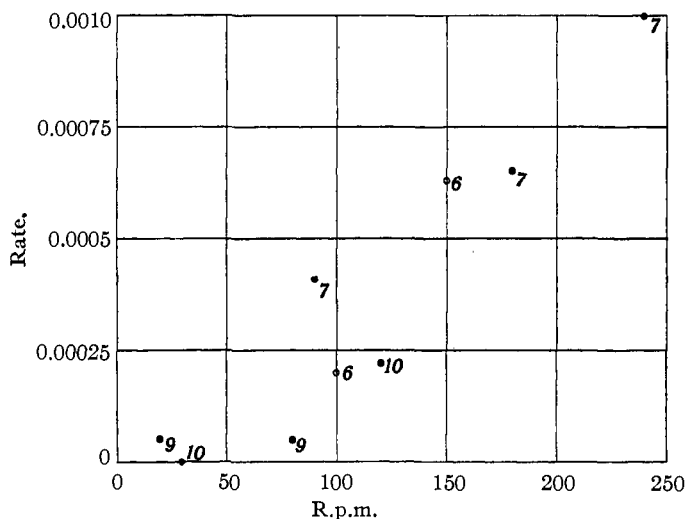


Fig. 1.

the single runs. The complete data for run 7, which is fairly typical, are shown in Fig. 2. We did not work at greater rates than 250 r.p.m. because at that rate the stirring had become rather violent; it is scarcely possible to suppose that such agitation is not much more than is needed to keep a fresh supply of reactants at the surface and the increase in rate which occurs with increased stirring in this region is probably due to

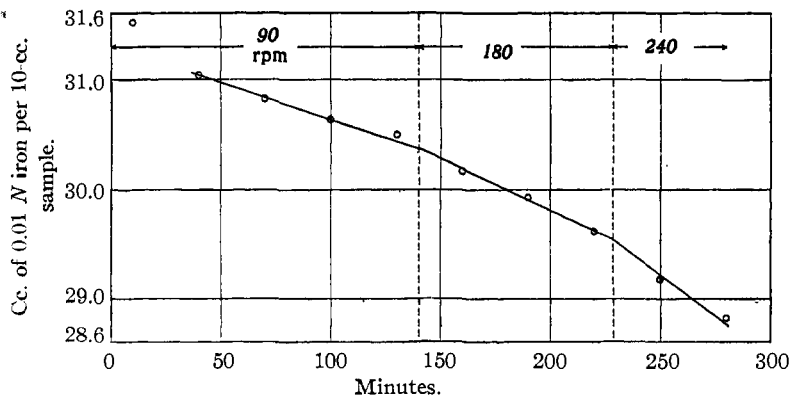


Fig. 2.

a breakdown in the oriented absorption of *A*, giving a condition more favorable to reaction, or to incipient emulsification, with a consequent increase in the area of the interface; that this last suggestion is not unreasonable follows from the fact that visible emulsification occurs at rates of about 500 r.p.m.

The remaining runs were devoted to a determination of the temperature coefficient of the reaction rate at about 120 r.p.m. Runs 13-16 were made with Sample II and runs 17-20 with Sample III. The temperature range of the former series was only 30-40° and the stirring was somewhat erratic. The results confirm those of the latter series but cannot be regarded as very reliable. Runs 17-20 were all very good and the technique of regulating the stirrer had been mastered by then. The sample used was the best of the three; it reacted more slowly than did Sample II, and the rates, therefore, apply to the initial part of the reaction when only a small amount of manganese dioxide was present. The separate

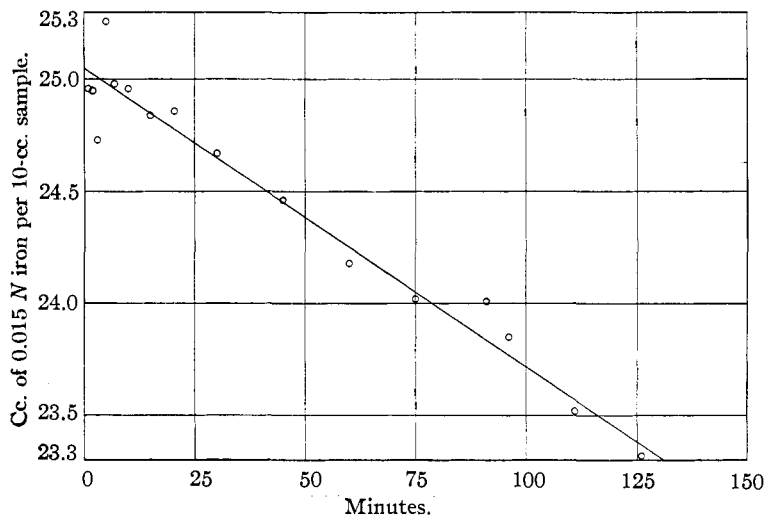


Fig. 3.

titrations with few exceptions were in good agreement and the determination of the rate from the slope of a straight line drawn through the experimental points was subject to an uncertainty of not more than 5%. The complete data for run 18 are shown in Fig. 3, and the results for the entire series are listed in Table I.

TABLE I
RESULTS FOR THE SERIES

Run number	17	18	19	20
Temperature, °C.	25.6	45.3	35.15	15.3
k	0.00025	0.00120	0.00052	0.000126

In this table k is the number of moles of permanganate reduced per hour per cm.² of surface per unit molarity of the permanganate, with 6 g./liter of A in the benzene solution, at 120 r.p.m. with the stirrer described.

In Fig. 4 is shown a plot of $\ln k$ against $1/T$ for these values. The four points lie on a smooth curve which, however, is not a straight line. The

curvature is not great but is far from negligible, as a calculation of the energy of activation E_0 for various intervals shows.

TABLE II

VALUES OF E_0

Temperature interval, °C.	15.3-25.6	25.6-35.15	35.15-45.3
E_0	11,500	14,100	16,200

These values are all subject to a correction of $RT/2$ if the reaction is bimolecular, but this is in any case negligible.

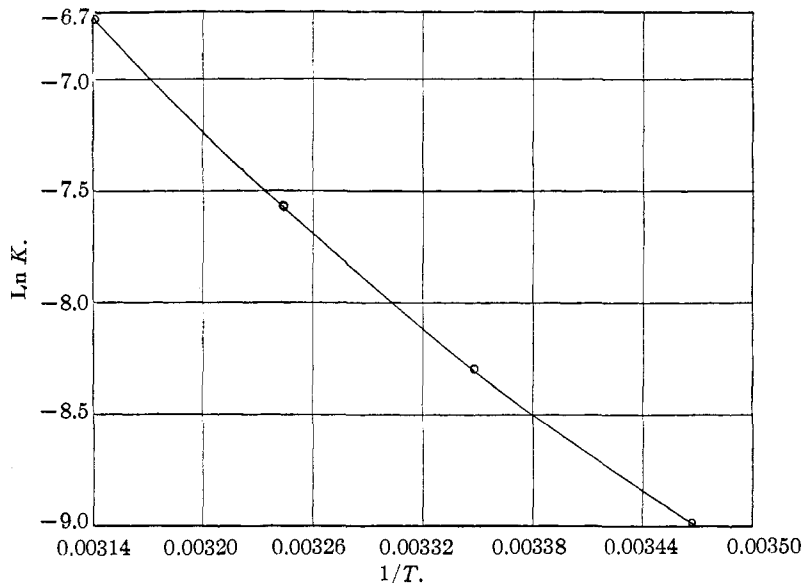


Fig. 4.

Discussion

If this trend in the value of E_0 is real, as we believe it to be, there are a number of possible explanations for it. The reaction product, B , is not perfectly stable to permanganate, and there may be a slow but appreciable homogeneous reaction occurring, particularly at the higher temperatures. This could result in a trend of the sort observed if the homogeneous reaction had the larger temperature coefficient. Or, since A is distinctly soluble in boiling water, it may not be quite insoluble at 35-45°. Thus, there may be a certain amount of homogeneous oxidation of A in addition to the main heterogeneous part of the reaction. This would lead to a trend of the type observed, regardless of which reaction had the greater temperature coefficient, but it would seem very likely, if this explanation is correct, that the larger one belongs to the homogeneous reaction, first because that is the normal situation, and second because in this case the temperature

coefficient for the homogeneous reaction would include the temperature coefficient of solubility. Then the energy of activation for the interfacial reaction would be less than 11,500, and that for the homogeneous reaction greater than 16,200. Other explanations for this trend in E_0 are possible; in fact, any two or more reactions, either simultaneous or successive, both leading to a reduction of permanganate, are capable of accounting for it.

It is not possible from the results of our work to assert definitely what the cause of the disagreement between our results and those of Bell is, but we believe that the following reason will probably account for it. Bell says (p. 883), "One preparation was recrystallized from alcohol and one from benzene. . . . Both were therefore considered pure and were used indifferently in the subsequent work." The first series of Bell's runs (Runs 5-16) is devoted to a determination of the dependence of the reaction rate on the concentrations. The first three of these, taken alone, show the reaction to be first order with respect to the permanganate; the last six, made at approximately constant permanganate concentration, give a smooth curve when the rate is plotted against the concentration of A . The velocity read from the curve for 4.55 g./liter of A is 3.3 cc./hour. The first three runs of the series were made at 4.55 g./liter of A , and when corrected to the same permanganate concentration as the other six give, in the same units, a rate of 0.56 cc./hour. The discrepancy, a factor of 6, is scarcely assignable to experimental error in view of the good agreement within each of the two groups. Bell does not mention this disagreement at all; since our own three samples showed considerable differences in rate, we consider it probable that the same is true of the two Bell used, and that the first three runs of this series were made with the less active sample. It is worth noticing that if his temperature coefficient, 13, be divided by this ratio, $3.3/0.56$, the result is 2.2 in very good agreement with our own value of 2.0 for the same temperature interval. If this suggestion as to the cause of his error is correct, then he must have made Runs 5, 7, 8 of Series 1 and all those of Series 3 with a single sample, the less active one; and must have made the remaining runs of Series 1 and all those of Series 2 with the more active sample.⁶

With regard to the actual nature of the catalyst responsible for the varying activity of the different preparations, we have no suggestion to

⁶ Bell has informed us that the explanation we suggest is not acceptable. It seems that the runs for which the reported concentration of A was 4.55 g./liter were made at an actual concentration of 1.55 g./liter. This removes the factor of six pointed out above. Furthermore, all the runs on which the temperature coefficient was based were made with a single sample. Bell is willing, however, to accept our value for the temperature coefficient, since his study of this quantity was a minor point in his investigation. We wish to emphasize that the main thesis of his work, the verification of the Gibbs-Helmholtz equation, is not affected by our work.

make. Of our three samples, I was about twice as active as III and II 5-7 times as active.

It may be worth while to repeat the calculation which Bell has given for the fraction of fruitful collisions of permanganate ions at the interface. This is necessarily based on the unlikely assumption that the ions may be treated as a perfect gas. It is found that at 25°, making this assumption, 2.07×10^4 moles would strike per cm^2 per hour per unit molarity, and of these 0.00025 moles would react. The fraction of fruitful collisions is, therefore, 1.2×10^{-8} , about one-tenth that Bell found; in the absence of knowledge as to the rate of stirring that he used this is not very significant, though it points to a somewhat lower rate for our Sample III than for either of his. If we put $1.2 \times 10^{-8} = e^{-E_0/RT}$ and solve for E_0 , we get 10,900 calories. This value is not very significant. The calculated number of molecules striking is quite possibly in error by a large factor, due to negative adsorption among other causes; the chances are that it is too large. This would mean that the true fraction of fruitful collisions is greater than that calculated, and the corresponding true value of E_0 would be smaller. However, the direct calculation of E_0 in this way is rather naïve. It has been suspected for a long time, and the great mass of experimental data of Hinshelwood and others show it to be so, that the rate of a bimolecular gas reaction is calculable by multiplication of the number of collisions with the factor $e^{-E_0/RT}$; but there is no certainty that the actual mechanism of the reaction considered here is bimolecular (for example, it might involve the unimolecular breakdown of a complex formed between A and a permanganate ion) and furthermore the work of Norrish and Smith⁷ shows that for reactions occurring in solution it is necessary to introduce a probability factor P , which may be very small. The omission of this factor, if it should be present, would make the calculated value of E_0 too large. There are thus at least two sources of error, both tending to make the calculated value of E_0 too large, so that the true value is probably less than 10,900 by a considerable amount, although some unsuspected error in the other direction may change this. The value with which this calculated quantity is to be compared is also uncertain. If, as has been said was possible, the trend in the observed temperature coefficient is due to two reactions occurring together, that with the lower temperature coefficient being heterogeneous, then the energy of activation for the heterogeneous reaction is less than 11,500. In fact, on this basis, we should be justified in applying the $RT/2$ correction mentioned before and saying that it was less than 11,200. It is quite possible for a number less than 10,900 to equal a number less than 11,200, but this possibility does not lend any weight to the vast number of assumptions made in arriving at these figures. There is no large obvious discrepancy,

⁷ Norrish and Smith, *J. Chem. Soc.*, 1928, 129.

such as Bell's work appeared to involve, but more than that cannot be said. It is, of course, needless to mention that the close agreement between the numbers 10,900 and 11,200 is to be regarded as a coincidence without significance. There are several other causes which contribute to the uncertainty of the foregoing calculations. Among these are a possible variation of the concentration of the adsorbed film of *A* with the temperature and the effect of the catalyst. It would be possible to clear up some of these points by further experimental work, but many of them seem destined to remain obscure unless information can be obtained from other measurements than those of reaction rates.

Conclusion

The general impression given by Bell's experimental results is that his work is reliable. On the whole his data are more consistent than our own. We therefore have felt safe in accepting, without verification, his results on the order of the reaction. His interpretation of the main reaction as being due to collisions of permanganate ions on the adsorbed film of *A* is inherently reasonable, and is not in disagreement with the very uncertain calculations of the last section. There does not seem to us, however, to be any certainty that it is correct. The trend in the temperature coefficient which we found probably means that there is some additional reaction occurring, but it is not possible to assert anything as to its nature. Much could be done by varying the depth of the aqueous layer, keeping other conditions constant. If the disturbing reaction is the subsequent oxidation of *B* homogeneously, this should change the disturbance and the main reaction by the same factor, leaving their ratio unchanged, while if there is a homogeneous oxidation of *A* it would increase in importance with the depth of the layer. Also, of course, the homogeneous oxidation of *A* could be increased, if it occurs, by increasing the concentration of *A*, best at a fairly high temperature. It should be remembered too that none of the existing derivations of the equation $(d \ln k/dT) = E_0/RT^2$ is directly applicable to a system in which the rate depends on the stirring, and that possibly the trend in the value of E_0 is normal. It does not seem to us, however, that the reaction is one which would repay further study; its twofold dependence on stirring and on an unknown catalyst make it rather unpromising from a theoretical standpoint, and, therefore, we do not intend to study the system further.

This investigation was aided financially from a grant made to Professor A. A. Noyes by the Carnegie Institution of Washington.

Summary

1. The oxidation of benzoyl-*o*-toluidine by permanganate at a benzene-water interface is dependent upon the rate of stirring and upon the presence of some unknown catalyst.

2. The temperature coefficient of this rate does not appear to be 13, as Bell reported, but, when runs under comparable conditions are made, is about 2. It increases somewhat with the temperature, indicating that more than one reaction is occurring.

3. The mechanism suggested by Bell, impact of permanganate ions on an adsorbed film of benzoyl-*o*-toluidine, does not disagree with the data, but it is impossible to make any but the crudest sort of verification. Other mechanisms are possible.

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[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 186]

A TEST OF THE RADIATION HYPOTHESIS OF CHEMICAL REACTION¹

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The viewpoint that thermal unimolecular reactions are to be considered as photochemical reactions with the activating frequencies lying in the infra-red region should be susceptible of experimental test by subjecting a system to radiation from an outside source and determining whether or not the thermal reaction rate is thereby increased. The difficulties in such an experiment arise from two sources. First, there is the necessity of obtaining a high intensity of infra-red radiation, without at the same time raising the temperature of the reacting substance to such a point that the normal thermal rate is the preponderating effect. In the second place, the extreme opacity of almost all substances to all but the shortest of infra-red rays makes it difficult to find a window that will permit a high intensity over the wide range of frequencies which may be important in activating the molecules. For since we do not know in what part of the infra-red spectrum the activating frequencies might lie, a conclusive test of the hypothesis should involve the use of all frequencies which are present to an appreciable extent in a hohlraum at the thermal reacting temperature.

Daniels³ has shown that over a considerable range of frequencies the unimolecular rate of decomposition of N_2O_5 is not appreciably affected by radiation. In the present experiments the effect of infra-red radiation on the rate of racemization of *d*-pinene in the liquid state was studied.

¹ Presented before the regional meeting of the Pacific Division of the American Association for the Advancement of Science, June, 1928.

² This is part of a thesis submitted by William Ure to the Division of Chemistry, California Institute of Technology, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

³ Daniels, *THIS JOURNAL*, **48**, 607 (1926).