but we have no information as to the exact states of our palladium catalysts. Variations in hydrogen *absorption* may be responsible for some of the variations in exchange patterns. On the whole, however, variations in exchange patterns were minor.

Relative Rates of Exchange.—The rate of production of exchanged hydrocarbon molecules of all degrees of exchange is equal to the rate of adsorption of hydrocarbon. The relative rates of exchange listed in Table I provide some information as to the nature of the transition state in this process.

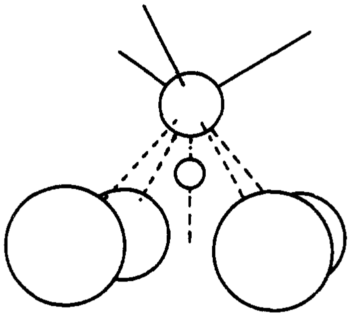

Fig. 5.—Possible transition state separating alkane (v) and monoadsorbed alkane.

In part, high reactivity seems to be correlated with low bond dissociation energies.[14] Hydrocarbons with only primary hydrogen atoms react slowly: methane and ethane,[15] neopentane.[3,16] Secondary hydrogen atoms in propane exchange more rapidly than the primary ones.[17] The tertiary hydrogen atom in isobutane exchanges rapidly.[17]

The sequence cycloheptane > cyclopentane > cyclohexane suggests that the transition state provides some relief from the strain occasioned by eclipsed hydrogen atoms.[18] Bonding of monoadsorbed alkane by multiple partial bonds as in interstitial carbides could account for this. A possible transition state is shown in Fig. 5 in which the separated hydrogen atom initially proceeds to below the surface.[19] Alternatively the hydrogen atom might move sidewise with a geometry somewhat resembling that of an S$_N$i reaction.

The larger number of partial bonds in the eclipsed than in the staggered *vic*-diadsorbed alkane would stabilize the eclipsed conformation.

We have postponed until this place a possible objection to an eclipsed *vic*-diadsorbed species. 2,3-Dimethylbutane exhibits an isotopic exchange pattern little different from that of hexane or 3-methylhexane. For exchange beyond seven hydrogen atoms in one adsorption step with 2,3-dimethylbutane, one requires 2,3-diadsorbed-2,3-dimethylbutane which involves two sets of eclipsed methyl groups. Perhaps, however, the enthalpy of adsorption at two tertiary positions compensates for the additional eclipsing strain.

Acknowledgment.—This research was supported by the Office of Naval Research. We are indebted to Dr. K. W. Greenlee, American Petroleum Institute, Project 45, at the Ohio State University for the sample of 1,1-dimethylcyclopentane.

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[14] A. F. Trotman-Dickenson, "Gas Kinetics," Butterworth Scientific Publications, London, 1955, p. 15.

[15] K. Morikawa, N. R. Trenner and H. S. Taylor, THIS JOURNAL, **59**, 1103 (1937).

[16] C. Kemball, *Trans. Faraday Soc.*, **50**, 1344 (1954).

[17] C. Kemball, *Proc. Roy. Soc.* (*London*), **223A**, 377 (1954).

[18] H. C. Brown, R. S. Fletcher and R. B. Johannesen, THIS JOURNAL, **73**, 212 (1951).

[19] A similar proposal has been made for hydrogen chemisorption, M. E. Winfield, *Rev. Pure Appl. Chem.*, **5**, 217 (1955).

EVANSTON, ILLINOIS

[CONTRIBUTION FROM THE DEPARTMENT OF PHYSICAL CHEMISTRY, UNIVERSITY OF LEEDS]

Photochemical Technique

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The range of concentration and wave length over which a photochemical reaction can be studied usefully may be increased if a mirror is used to reflect transmitted light back into the reaction system. This makes the intensity distribution much more uniform and so allows a reaction not directly proportional to intensity to be studied at higher concentration than would otherwise be possible. The necessary theory and an experimental method for determining the reflectivity of the mirror is given.

1. Introduction

The range of concentration, or of wave length, over which a photochemical reaction can be studied is often quite severely limited by the optical properties of the light-absorbing species. At one limit absorption may be strong enough to cause a very non-uniform distribution of intensity, a most undesirable feature when the reaction rate is not directly proportional to intensity. At the other limit absorption may be so weak that it is difficult to obtain satisfactory rates with convenient intensities, or it may be necessary to decompose a significant proportion of the reactants if products are to be obtained in measurable quantities.

The main object of this paper is to show how the useful range of study may be extended by using a mirror to reflect transmitted light back into the reaction medium. This gives a gain of intensity at low absorptions, but also has the more important effect of greatly increasing the uniformity when the

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[1] (a) Atomic Energy of Canada Ltd., Chalk River, Ontario, Canada. (b) Plastics Division, Imperial Chemical Industries, Ltd., Welwyn Garden City, Herts, England.

absorption is quite large, so permitting work at higher extinction coefficients than would otherwise be possible. The reflectivity of the mirror cannot be calculated satisfactorily and a method for determining this experimentally using an actinometer in which only part of the light is absorbed is given. At low concentrations it is necessary to correct for slight decomposition of the actinometric species.

2. **Reflection Corrections.**—If a gas reaction is being studied, or if a mirror is used, the reflection of transmitted light cannot be neglected and it is necessary to know the ratio of absorbed to incident intensity as a function of the optical density of the reactants and the reflection coefficients of the interfaces. The latter can be calculated from Fresnel's law or, for a mirror, measured experimentally by the method described later. The formulas for two optical arrangements are given in this section

(a) For a cell with two parallel plane faces, d cm. apart, in a beam of parallel monochromatic light incident normally on one face. If ϵ is the molar extinction coefficient of the light-absorbing species and c the concentration, the fraction of light absorbed in a single passage through the cell contents is $(1 - S)$ where

$$S = e^{-\mu c} \qquad \mu = 2.303\epsilon d \qquad (2.01)$$

Suppose that the intensity entering the cell contents directly from the source is I_0, this being the quantity measured by a total absorption actinometer, that fractions r_1 and r_2 incident on the insides of the faces nearer and farther away from the source are reflected back into the cell, and that a fraction τ of the light incident on the inside of the face farther from the cell is transmitted. r_1, r_2 and τ may be composite quantities including reflections from surfaces parallel to the faces of the cell, for example windows in a thermostat.

The intensity absorbed from the primary beam is $I_0(1 - S)$, leaving I_0S incident on the second face of the cell to give a reflected beam of initial intensity I_0r_2S. From the latter an intensity $I_0r_2S(1 - S)$ is absorbed. Proceeding in this way and summing the resulting series the total absorbed intensity is found to be

$$I_a = I_0\frac{(1 - S)(1 + r_2S)}{1 - r_1r_2S^2} = I_0F(S) \qquad (2.02)$$

and the transmitted intensity

$$I_T = I_0\frac{\tau S}{1 - r_1r_2S^2} \qquad (2.03)$$

When r_1 and r_2 are equal (2.02) and (2.03) reduce to the formulas obtained by Hunt and Hill.[2]

When r_1 and r_2 are known (2.03) generally can be applied because I_0 can be measured at most wave lengths by actinometry while S easily is calculated or measured on a spectrophotometer. When a mirror is used r_2 cannot be calculated from Fresnel's law for normal incidence, but can be determined experimentally by fitting (2.02) to a series of values of I_a and S for the actinometric solution if an accurate value is required. The potassium ferrioxalate actinometer recently developed by Parker[3] is suitable for this purpose.

(b) In many photochemical reactions it is difficult to obtain a high enough absorbed intensity while still retaining satisfactory optical conditions. This sometimes can be overcome by surrounding a cylindrical source with a coaxial annular vessel, end-effects being minimized by using a source longer than the cell and silvering the ends of the latter. If the diameter of the source is small compared with the inner diameter of the cell the light flux is radial.

Suppose the radii of the inner faces of the cell are x_1 and x_2 $(x_1 < x_2)$, that the corresponding reflection coefficients are r_1 and r_2, and that τ is now that fraction of light incident on the inner wall of the cell in the direction of decreasing x which is transmitted by this face and is incident on the opposite side of the cell after passing through the source. $(r_1 + \tau)$ is the effective reflection coefficient for the inner surface.

The intensity of the primary beam decreases in the positive x direction due to absorption and the increasing surface area giving

$$\frac{dI}{dx} = \frac{\partial I}{\partial x} + \frac{\partial I \partial A}{\partial A \partial x} \qquad A = 2\pi x \qquad (2.04)$$

Solving this equation, and that for the reverse direction, and summing corrections as in the previous example the absorbed intensity is found to be

$$I_a = \frac{I_0(1 - S)(1 + r_2S)}{1 - (r_1 + \tau)r_2S^2} \quad S = e^{-\mu(x_2 - x_1)} \qquad (2.05)$$

provided all intensities are reduced to the area of the inner surface of the cell, this being the area over which a total absorption actinometer would measure I_0. For an opaque source τ is zero and (2.05) reduces to (2.02). For a transparent source τ can approach unity and if r_2 is made large by silvering the outside of the cell I_a is nearly independent of S. Under these conditions most of the light is photochemically effective even though the cell contents may only absorb weakly.

The greater uniformity achieved by using a mirror can be simply demonstrated for case (a). Taking r_1 to be zero the change of intensity across the cell as a percentage of that at the face nearest the source is

$$\Delta = 100\left\{1 - \frac{(1 + r_2)S}{1 + r_2S^2}\right\} \qquad (2.06)$$

Figure 1 shows Δ as a function of S for r_2 equal to 0.90 and zero, corresponding to using the cell with and without a mirror. The improvement is marked and little affected by r_2 in the range 0.85 to 0.95. At 40% absorption the non-uniformity is only 10% when a mirror is used.

The remaining discussion in this paper applies to the optical arrangement (a). An almost identical treatment can be given for (b).

3. **Corrections for Finite Decomposition.**—I_a has been obtained as a function of S and the constants of the optical system. Since S changes during an experiment I_a also changes and it may be necessary to correct for this, the correction often being quite appreciable because many reactions have

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[2] Hunt and Hill, *J. Chem. Phys.*, **15**, 111 (1947).

[3] Parker, *Proc. Roy. Soc.* (*London*), **A220**, 104 (1953).

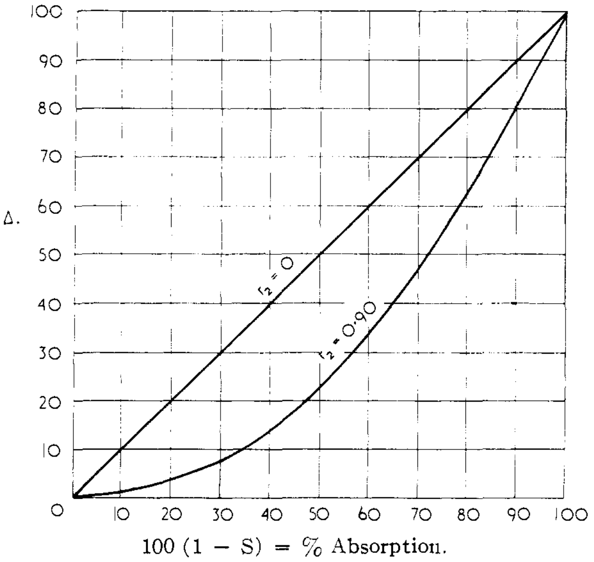

Fig. 1.

to be taken to 10% decomposition or more to obtain measurable quantities of the products.

The rate of change of the concentration of the light-absorbing species depends on I_a and hence is some function of S, say

$$-\frac{dc}{dt} = G(s) \qquad (3.01)$$

which can be combined with (2.01) to give

$$\frac{1}{S}\frac{dS}{dt} = \mu G(S) \qquad (3.02)$$

This can sometimes be integrated explicitly and in other cases a solution obtained as

$$\mu_t = \int_{S^0}^{S_t} \frac{dS}{SG(S)} \qquad (3.03)$$

where S_0 and S_t are the values of S at 0 and t. If $G(S)$ is known, (3.03) can be used to give the time variation of S and hence that of I_a. Alternatively if G contains an unknown, for example a rate constant or quantum yield for some step in a complex reaction, it may be used to obtain a value for this quantity by fitting (3.03) to experimental values of S and t.

4. Corrections in Actinometry.—For the particular case of a reaction proportional to intensity, for example the ferrioxalate actinometer

$$G(S) = \phi I_a \qquad (4.01)$$

where ϕ is the quantum yield and I_a is given by (2.02). Because $G(S)$ has this simple form, (3.02) can be solved explicitly for S. The extent of reaction is measured by some chemical change Q, given by

$$Q = \phi \int_0^T I_a\, dt = \phi \int_0^T I_0(t) F(S)\, dt \qquad (4.02)$$

There usually will be some fluctuation in the source intensity during an experiment and (4.02) should take account of variations both in I_0 and photolyte concentration. Provided not more than 10% decomposition occurs this is done by using a mean value of I_0 in (3.02) to obtain the variation of S with time, and then taking account of the fluctuations in I_0 when (4.02) is integrated. Writing

$$I_0(t) = \bar{I}_0 + i_0(t) \qquad \bar{I}_0 = \frac{1}{T}\int_0^T I_0(t)\, dt$$
$$(4.03)$$
$$F(S) = \bar{F}(S) + f(S),\ \bar{F}(S) = \frac{1}{T}\int_0^T F(S) dt$$

(4.02) becomes

$$\frac{Q}{T\phi} = \bar{I}_0\bar{F} + \frac{1}{T}\int_0^T i_0(t) f(S)\, dt \qquad (4.04)$$

Generally the integral in (4.04) can be neglected but this should be verified by calculating an upper limit to the error so introduced directly from the experimental data. Using Schwartz's inequality

$$\left[\int_0^T i_0(t) f(S)\, dt\right]^2 \leqslant \int_0^T i_0^2(t)\, dt \int_0^T f^2(S)\, dt \qquad (4.05)$$

but

$$\int_0^T i_0^2(t)\, dt = \int_0^T I_0^2(t)\, dt - T\bar{I}_0^2$$
$$\int_0^T f^2(t)\, dt < T \left\{F(S_0) - F(S_T)\right\}^2 \qquad (4.06)$$

where S_0 and S_T are the initial and final values of S. Combining (4.05) and (4.06)

$$\left|\int_0^T i_0(t) f(S)\, dt\right| < \{F(S_0) - F(S_T)\}$$
$$\left[T\int_0^T I_0^2\, dt - T^2\bar{I}_0^2\right]^{1/2} \qquad (4.07)$$

Using a mean value for I_0, the differential equation for S is

$$\frac{1}{S}\frac{dS}{dt} = \alpha F(S) \qquad \alpha = \mu\phi\bar{I}_0 \qquad (4.08)$$

This can be solved for S as a power series in t by standard methods,[4] but for variations in S of 10% or less a quadratic approximation is sufficient

$$S_t = S_0(1 + m_1 t + m_2 t^2) \qquad (4.09)$$

with

$$\left.\begin{aligned} m_1 &= \alpha F(S_0);\ m_2 = \frac{\alpha}{2T}\left\{S_T F(S_T) - S_0 F(S_0)\right\} \\ \alpha &= \frac{2(S_T - S_0)}{T\{S_0 F(S_0) + S_T F(S_T)\}} \text{ or by (4.08)} \end{aligned}\right\} \qquad (4.10)$$

This approximation may be applied with confidence when m_2/m_1 is small, and often m_2 can be neglected. When that is so $\bar{F}$ can be obtained as an explicit function of T.

Experimental

As noted above, one of the most useful applications of reflection corrections in photochenical studies is the use of a mirror to achieve more uniform intensity distribution across a reaction cell. It is the purpose of this section to show how experimental measurements with a chemical actinometer can be used to evaluate the reflection coefficient r_2 of the mirror, once the relative variation of quantum yield with concentration is known. The potassium ferrioxalate actinometer[3] was selected because of its great sensitivity.

Since the variation of the quantum yield ϕ with the concentration of potassium ferrioxalate had not previously been investigated over a sufficiently wide range, a preliminary series of runs was carried out without a mirror. In this case $r_1 = r_2$, and equation (2.02) becomes

$$I_a = \frac{I_0(1 - S)}{1 - r_1 S} \qquad (5.01)$$

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(4) H. Margenau and G. Murphy, "The Mathematics of Physics and Chemistry," D. Van Nostrand Co., New York, N. Y., 1943.

The rate of production of ferrous ion is given by ϕIa where ϕ is the quantum yield for the reduction of potassium ferrioxalate, and therefore

$$I_0 = \frac{I_a(1 - r_1S)}{(1 - S)} \qquad (5.02)$$

By measuring ϕIa as a function of S at constant I_0, the *relative* variation of ϕ with concentration of potassium ferrioxalate was determined. The reflection coefficient r_1 at a glass-water interface is very small (approximately 0.004) and can be calculated from Fresnel's law.

All photolyses were carried out in a cylindrical quartz cell, 1 cm. deep and 2 cm. in diameter. The cell was filled with potassium ferrioxalate solution of appropriate concentration, placed in a water thermostat at 25°, irradiated for a known time, and then analyzed spectrophotometrically for the amount of Fe^{++} produced. Runs were carried out in the presence of air and without stirring, but as the extent of reaction never exceeded 2% the accuracy of the measurements would not be affected. The analytical method suggested by Parker[3] was employed.

Monochromatic light of wave length 4358 A. was used. The light source was a Mazda 250 watt ME/D high pressure compact source lamp run at 60 volts and 3.6 amp. The voltage was stabilized electronically. The 4358 Å. group of lines was isolated by means of 2 cm. of $Cu(NO_3)_2$ solution and 1 cm. of $NaNO_2$ solution. In order to avoid reflections from the thermostat windows the bath was inclined at a slight angle to the incident beam, the reflected beam from the window falling onto a photocell, the output of which could be measured continuously with an electrometer triode and potentiometer circuit to ±0.3%. In this way it was possible to correct for small fluctuations in the incident light intensity I_0. Although a slow drift of 5–10% often occurred over a period of eight hours, the fluctuations from the mean during an individual run (15–30 min.) were usually less than 1%.

The potassium ferrioxalate concentration in 0.1 N sulfuric acid was varied from 0.17 M (at which $S = 0$), to 0.001 M (at which $S \sim 0.85$). A total of 24 separate runs were made. At the lower concentrations, it was necessary to apply small corrections for the amount of ferrioxalate decomposed during a run (see Sect. 4). No significant correlation was observed between the measured value of ϕI_0 and the concentration of potassium ferrioxalate, and therefore within the ±2% error of our results the quantum yield does not vary with concentration. A similar conclusion was recently reached by Hatchard and Parker.[5] I_0 was about 1.7×10^{11} quanta cm.$^{-2}$ sec.$^{-1}$.

A second set of photolyses was then carried out with a small mirror held by means of a spring clip against one of the optical faces of the cell. The ferrioxalate solution was successively diluted from 0.17 to 0.001 M, and the rate of production of ferrous ion (ϕI_a) measured as above.

From equation 2.02

$$\phi I_a = \frac{\phi I_0(1 - S)(1 + r_2S)}{1 - r_1r_2S^2} = \frac{\phi I_0(1 - S)(1 + r_2S)}{1 - 0.004r_2S^2} \qquad (5.03)$$

and therefore the reflection coefficient r_2 of the mirror may be determined by fitting the experimental values of ϕI_a and S to eq. 5.03 by the method of least squares. From a typical series of runs the optimum value of r_2 was found to be 0.85, and a duplicate series gave 0.84, the agreement being rather better than can be expected. The mirror used in this work was not specially prepared and had visible imperfections in the reflecting surface. A reflection coefficient greater than 0.9 should be attainable readily.

Acknowledgment.—It is a pleasure to thank Professor F. S. Dainton for a suggestion which prompted this study and for his interest and encouragement during the work, and to acknowledge the awards of a Canadian Ramsay Memorial Fellowship and a Salters' Company Research Fellowship.

[5] Hatchard and Parker, *Proc. Roy. Soc. (London)*, **A235**, 518 (1956).

LEEDS, ENGLAND

[CONTRIBUTION FROM THE DEPARTMENT OF PHYSICAL CHEMISTRY, UNIVERSITY OF LEEDS]

The Photolysis of Saturated Aldehydes and Ketones

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An analysis of the structure of the carbonyl group is used as a basis for the understanding of the important primary processes in the photolysis of saturated aldehydes and ketones, with particular reference to molecules containing propyl and larger alkyl groups. The close correlation between the photolysis products from the ketones and their electron impact fragmentation patterns is accounted for.

1. Introduction

The photolysis of saturated aldehydes and ketones has been studied widely in the quartz ultraviolet region and, to a lesser extent, at shorter wave lengths. Although the important primary processes are now known, and are understood in large measure, it has not been possible to relate all features of the decompositions to molecular structure and the electronic changes resulting from the absorption of light. In particular, rather unexpected rearrangements occur when alkyl groups with three or more carbon atoms are present. Recently Nicholson[2] has found, for a series of ketones, that these rearrangements show a striking correlation with the electron-impact fragmentation patterns.

The long-wave absorption of aldehydes and ketones is due to the excitation of a loosely bound lone-pair electron on the oxygen, this excitation leading to decomposition either by the breaking of a C–C bond adjacent to the carbonyl group to give two radical fragments or by a variety of intermolecular rearrangements to give normal molecules directly. Radical and molecular decompositions may occur simultaneously, even when only one electronic transition is involved.

2. Electronic Structure of CO and the Carbonyl Group.—The electronic structure of the carbonyl group has been discussed by Mulliken,[3] McMurry[4] and Walsh,[5] all these authors reaching essentially the same conclusion. Sahni's[6] recent application

[1] Imperial Chemical Industries Ltd., Plastics Division, Welwyn Garden City, Herts., England.

[2] A. J. C. Nicholson, *Trans. Faraday Soc.*, **50**, 1067 (1954).

[3] R. S. Mulliken, *J. Chem. Phys.*, **3**, 564 (1935).

[4] H. L. McMurray, *ibid.*, **9**, 231 (1941).

[5] A. D. Walsh, *J. Chem. Soc.*, 2306 (1953).

[6] R. C. Sahni, *Trans. Faraday Soc.*, **49**, 1246 (1953).