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

BY P. P. MANNING[1]

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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

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[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).

of an atomic orbital molecular orbital theory to CO can be used as a basis for a description of the carbonyl group which gives a confirmation of earlier work, but founded on more detailed calculation than has been possible before. The structure of CO makes a satisfactory starting point for discussion of the electronic structure of aldehydes and ketones because the non-polar alkyl groups introduce localized forces only, these modifying the C–O bond in a substantial but clear-cut way. On going from CO to the molecule R_1R_2CO the σ-bonding orbital $t\sigma$, the oxygen lone-pair orbital $s\sigma$, and one π-bonding orbital (π_x) are not directly affected by the C–R bonds and will be largely unchanged. However, the carbon lone-pair orbital $u\sigma$, and the π_y bonding and antibonding orbitals are greatly altered. The latter are replaced by two more localized orbitals of which the first is largely in the carbon half of the bond and combines with $u\sigma$ in the C–R bond orbitals, and the second, say y_0, is largely near the oxygen and roughly resembles the $2p_y$ orbital on that atom. The orbital y_0 is doubly occupied and represents a lone-pair on the oxygen with a node on the C–O axis, this node and the localization making these electrons more weakly bound than any in CO. Sahni's calculations show that the π_x orbital is weighted toward the oxygen and that correspondingly the unoccupied orbital π_x^* is weighted toward the carbon, a feature which had been deduced earlier by Walsh.[5] This asymmetry plays a very important part in the photodecompositions.

3. **Ionization Potentials and Spectra.**—Saturated carbonyl compounds have a first ionization potential at a little over 10 e.v. corresponding to ionization from y_0.[3]

The long-wave absorption at about 2900 Å. is the main region of photochemical interest and so its correct interpretation is of some importance. There seems little doubt that this is the singlet–singlet transition of an electron from y_0 to an orbital resembling π_x^*.[3–5] Since the band has a molar extinction coefficient of about 10 at the maximum it is too strong to be a singlet–triplet transition in a molecule containing light atoms only, though there is a slight shoulder on the long-wave side which has been interpreted as this.[7,8] If the main absorption is the associated singlet–singlet transition this interpretation seems unlikely because a greater separation would be expected, as indeed occurs for acetone where a long-lived fluorescence at 3850–5000 Å. seems reliably identified as a triplet–singlet emission.[9–11] Probably the shoulder is of vibrational origin and the whole band can be assigned to the excitation of an electron from y_0 to the π_x^* antibonding orbital. This transition is symmetry-forbidden in the equilibrium configuration but becomes allowed when buckling about the carbonyl carbon occurs, the observed intensity being as expected under these circumstances. The excited orbital will not be very close to the π_x^* orbital of CO but there will be some transfer of electronic charge from the oxygen to the carbon.[5] This increase of electron density about the carbonyl carbon will weaken the C–R bonds, and if dissociation occurs it is to be expected at these rather than the stronger C–O bond. Walsh[5] has pointed out that the equilibrium configuration in the upper state may be slightly buckled. More important, from a photochemical point of view, the lowered force constants in the upper state will facilitate buckling and bending about the carbonyl carbon, and large amplitudes in these modes are likely because they provide the asymmetry which makes the electronic transition possible, so giving considerable opportunity for intramolecular rearrangement. Experimentally both dissociation at the C–R bonds and intramolecular rearrangements are observed.

4. **Photolysis of Aldehydes and Ketones.**—This section is mainly concerned with the primary processes for aldehydes and ketones with an alkyl group of more than two carbon atoms. A detailed account of earlier work, particularly that on the lower aldehydes and ketones, is given by Steacie.[12]

Aldehydes.—For acetaldehyde earlier work has shown that at 3130 Å. the only important primary step is

$$CH_3CHO + h\nu \longrightarrow CH_3\cdot + CHO\cdot \qquad (4.01)$$

but, if results from the iodine-inhibited reaction are reliable, the intramolecular process

$$CH_3CHO + h\nu \longrightarrow CH_4 + CO \qquad (4.02)$$

becomes of increasing importance at shorter wave lengths,[13] and on going from 3130 to 2380 Å. the products indicate increasing vibration in modes which bring the hydrogen near the methyl group. Similar trends have been found for propionaldehyde and n-butyraldehyde,[14] these results being confirmed by Blacet and Crane,[15] who found the same behavior for isobutyraldehyde, but did also detect significant amounts of ethylene in the products from n-butyraldehyde for which they were not able to account. Evidence from the ketone series, given below, strongly suggests that the ethylene is produced by the primary step

$$CH_3CH_2CH_2CHO + h\nu \longrightarrow CH_2{=}CH_2 + CH_3CHO \qquad (4.03)$$

The authors do not give acetaldehyde as a product but it would be difficult to detect in the presence of much butyraldehyde.

Ketones.—Acetone and methyl ethyl ketone decompose by a primary split into free radicals but higher ketones produce considerable amounts of olefin by a molecular process which competes with the radical decomposition. Davis and Noyes[16] have shown this for methyl n-butyl ketone, the decomposition being largely represented by the equation

$$CH_3COC_4H_9 + h\nu \longrightarrow CH_3CO_2CH_3 + CH_2{=}CHCH_3 \qquad (4.04)$$

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(7) A. D. Walsh, *J. Chem. Soc.*, 2318 (1953).

(8) S. A. Schou, *J. chim. phys.*, **26**, 24, 27 (1929).

(9) W. A. Noyes. Jr., *J. Phys. Chem.*, **52**, 546 (1948).

(10) G. W. Luckey and W. A. Noyes, Jr., *J. Chem. Phys.*, **19**, 227 (1951).

(11) D. S. McClure, *ibid.*, **17**, 905 (1949).

(12) E. W. R. Steacie, "Atomic and Free Radical Reactions," Reinhold Publishing Corp., New York, N. Y., 1954.

(13) F. E. Blacet and D. E. Loeffler, THIS JOURNAL, **64**, 893 (1942).

(14) F. E. Blacet and J. N. Pitts, Jr., *ibid.*, **74**, 3382 (1952).

(15) F. E. Blacet and R. A. Crane, *ibid.*, **76**, 5337 (1954).

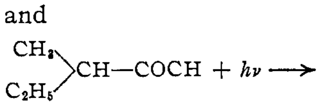
(16) W. Davis, Jr., and W. A. Noyes, Jr., *ibid.*, **69**, 2153 (1947).

and have suggested that this might be a cyclic rearrangement, though there appeared to be no likely reason for it. Similar results are found for dipropyl ketone.[17]

These surprising but well-established results have been confirmed recently by Nicholson[2] for the ketones CH_3COR where R is *n*-propyl, *n*-butyl, *n*-amyl, isopropyl and *sec*-butyl. In addition to the expected radical decomposition all except the isopropyl compound decomposed by intramolecular processes according to

$$\left.\begin{matrix} C_3H_7COCH_3 \\ C_4H_9COCH_3 \\ C_5H_{11}COCH_3 \end{matrix}\right\} + h\nu \longrightarrow \left\{\begin{matrix} CH_2{=}CH_2 \\ CH_3CH{=}CH_2 \\ C_3H_7CH{=}CH_2 \end{matrix}\right\} + CH_3COCH_3 \quad (4.05)$$

and



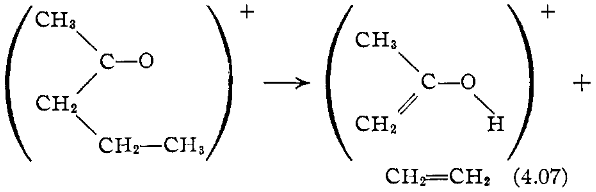
$$\begin{matrix} CH_3 \\ C_2H_5 \end{matrix}\!\!>\!CH{-}COCH_3 + h\nu \longrightarrow CH_2{=}CH_2 + C_2H_5COCH_3 \quad (4.06)$$

These are exact parallels to (4.03).

Nicholson also investigated the electron impact fragmentation patterns at the ionization potential of y_0 and found a close correspondence between the results and (4.05) and (4.06). In all cases the largest peak was at mass 43 (acetyl), and a significant peak occurred at mass 58 except when R was isopropyl or *sec*-butyl. Mass 58 must be formed by rearrangement and was attributed to acetone. No unexpected fragments were observed from methyl isopropyl ketone, while methyl *sec*-butyl ketone gave a peak at mass 72, attributed to methyl ethyl ketone, instead of one at 58. The rearrangements can occur both on photolysis and ionization, though at first it seems surprising that energy absorptions so characteristic of the carbonyl group should produce such profound changes in the region C_1 to C_3.

Light absorption and ionization involve a y_0 electron and both cause a loss of electronic charge from the neighborhood of the oxygen which favors movements of the nuclei giving an increase of electron density near it. In the photolysis the electron is partly removed to the carbonyl carbon and high angular distortions about that atom are favored.

By using atomic models it is seen that hydrogens on C_2, C_3, and C_4 can all approach the oxygen from the lone-pair direction. Since the field near the oxygen is strong it seems likely that the transfer of a hydrogen from C_3 to the oxygen occurs, the transfer being from C_3 because this, when combined with a simultaneous break between C_1 and C_2, gives more stable products than can be formed in any other way. For the methyl propyl ketone ion the result would be



(4.07)

with a similar mechanism for the polar state produced by photolysis. The positive charge is expected on the acetone fragment because conjugation in the system CH_2–C–O will delocalize it. Consideration of the symmetries of the orbitals during the rearrangement shows that the olefin will be in the lowest electronic state.

The cyclic rearrangement (4.07) accounts for Nicholson's results in all cases and seems quite reasonable when the effect of the positive charge in the neighborhood of the oxygen is considered.

It is a pleasure to thank Professor F. S. Dainton for much help and encouragement during the course of this work, Dr. E. Collinson for a useful discussion, and the Salters' Company for the award of a Research Fellowship.

LEEDS 2, ENGLAND

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[17] C. R. Masson, THIS JOURNAL, **74**, 4731 (1952).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING AND THE RADIATION LABORATORY, UNIVERSITY OF CALIFORNIA, BERKELEY]

Nuclear Magnetic Resonance Studies of the Aluminum Fluoride Complexes

BY ROBERT E. CONNICK AND RICHARD E. POULSON

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The nuclear magnetic resonances of F^{19} and Al^{27} were studied in solutions containing sodium fluoride and aluminum nitrate. The complex ions AlF^{++} and AlF_2^+ could be detected through their separate fluorine resonances and the measured concentrations agreed well with those calculated from the stability constants reported by Brosset and Orring. Only a single resonance was observed in solutions containing the higher complexes. The Al^{27} resonance appeared to be greatly broadened when the aluminum was complexed, presumably because of the coupling of the quadrupole moment with the unsymmetrical electric field. Measurements of the resonance of uncomplexed aluminum ion gave concentrations of Al^{+3} which again agreed well with those predicted from Brosset and Orring's data. From the difference in shielding of F^{19} in AlF^{++} and AlF_2^+ a lower limit was set on the lifetime for exchange of fluorines between these species. Similarly from the width of the aluminum resonance a lower limit could be set on the lifetime for exchange between Al^{+3} and the complexes.

The nuclear magnetic resonance of the fluorine atom is relatively sharp and readily detected. Therefore it is a potentially useful tool in studying the aqueous complexes of fluoride ions with various metal ions. To test the method an investigation was made of the nuclear magnetic resonance of fluorine in solutions containing sodium fluoride and aluminum ions. The complexing in this system has been studied previously by Brosset and Orring[1]

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[1] C. Brosset and J. Orring, *Svensk. Kem. Tid.*, **55**, 101 (1943).