tion. The slightly lower effect of the 4-fluoro atom may be due to the contribution of a stabilizing resonance

$$C\text{—}^-$$

form, $O=C\text{—}C=F^+$, not possible with a 2-fluoro group. The spectral shifts of the carbonyl group due to the introduction of a γ-fluoro atom into an α,β-unsaturated ketone and the relatively greater effect of an axial substituent have been recognized and explained[3] on the basis of prevention of double-bond polarization. In the present study the 6α-fluoro (equatorial) substituent caused a 10-fold shift in K_{eq} and the 6β-fluoro (axial) group a 40-fold shift or a net destabilization of the unsaturated ketone of 1.5 and 2.3 kcal., respectively. The general parallel between the position of the carbonyl frequency in the infrared and the position of the ketone–alcohol equilibrium (Table I) is worthy of note and supports the contention that the primary effect observed is one of ketone destabilization.

Enzymatic reductions[10] which have demonstrated the facile formation of Δ^4-3-ols from the halogenated unsaturated ketones may now be reinterpreted, in part, to include equilibrium considerations, although the electronic factors leading to high equilibrium concentrations of allyl alcohols appear to be the same as those promoting fast hydride transfer from reduced pyridine nucleotides.

(10) H. J. Ringold, S. Ramachandran, and E. Forchielli, *Biochim. Biophys. Acta*, **82**, 143 (1964).

WORCESTER FOUNDATION FOR   HOWARD J. RINGOLD
EXPERIMENTAL BIOLOGY   HAROLD LAWRENCE, JR.
SHREWSBURY, MASSACHUSETTS   J. M. H. GRAVES

The Effect of Pressure on the Rate of Hydrolysis of Chloroform. The Nature of the Transition State

Sir:

The dissociation of CCl_3^- to chloride ion and dichlorocarbene is commonly assumed to be the rate-controlling step in the basic hydrolysis of chloroform.[1] The possibility that the chloride ion might be displaced by water has been mentioned by Hine[2]; on the basis of kinetic arguments this path was held to be an unlikely one, although it could not be ruled out. More recently, a study of the base-promoted methanolysis of chloroform[3] showed k_2 to be proportional to h_-. However, the use of acidity functions in assessing the role of solvent molecules is at best highly uncertain, and it remains therefore an open question whether the solvent is to any degree involved in the formation of the intermediate.

Whalley, *et al.*,[4] and the present authors[5] have found knowledge of ΔV^* to be helpful in solving similar problems involving acid catalysis. It therefore appeared to us that a measurement of the pressure coefficient of the rate constant in the hydrolysis of chloroform would reveal to what extent water is involved in the

(1) J. Hine, "Divalent Carbon," The Ronald Press Company, New York, N. Y., 1964, pp. 36–42.
(2) J. Hine, *J. Am. Chem. Soc.*, **72**, 2438 (1950).
(3) R. A. M. O'Ferrall and J. H. Ridd, *J. Chem. Soc.*, 5035 (1963).
(4) For several references, see E. Whalley, "Advances in Physical Organic Chemistry," Vol. 2, V. Gold, Ed., Academic Press, Inc., New York, N. Y., 1964.
(5) W. le Noble and M. Duffy, *J. Phys. Chem.*, **68**, 619 (1964).

rate-determining step in that reaction. As before, any such participation is expected to lead to a negative activation volume, whereas simple dissociation would be characterized by a volume expansion. The data, essentially obtained by techniques described earlier,[6] are shown in Table I.

TABLE I

THE EFFECT OF PRESSURE ON THE RATE OF BASIC HYDROLYSIS OF CHLOROFORM AT 25° IN WATER CONTAINING 3% METHANOL

Pressure, kbar	$k_2 \times 10^5$, 1/mole sec.	Number of observations[a]
0.00	7.39	5
1.07	3.53	4
2.13	2.15	4
3.17	1.62	4
4.21	1.08	4
5.24	0.66	4
6.45	0.70	4

[a] The reaction was followed to about 70% completion; the rate constants were reproducible to about 5%. The base concentration was about 1; the chloroform concentration was below the saturation point by a factor of 10.

A plot of $\ln k_2$ vs. p yields a ΔV_0^* of $+16$ cm.^{3}/mole, by far the largest positive activation volume reported to date for a reaction in water.[7] This may be considered conclusive evidence that no water becomes bound in the transition state; the magnitude of the effect strongly suggests, in fact, that water electrostatically bound by the CCl_3^- ion is being released during the reaction and that the transition state goes on to free CCl_2. We are currently investigating other reactions assumed to go through carbene intermediates, and hope to report those results as well as some of the experimental details later.

(6) W. le Noble, *J. Am. Chem. Soc.*, **85**, 1470 (1963).
(7) This value is even more remarkable when it is remembered that ΔV^* tends to be smaller in highly polar solvents: K. R. Brower, *ibid.*, **85**, 1401 (1963).

DEPARTMENT OF CHEMISTRY   W. J. LE NOBLE
STATE UNIVERSITY OF NEW YORK AT STONY BROOK   M. DUFFY
STONY BROOK, NEW YORK

Photoelimination of Ethylene from 2-Pentanone[1]

Sir:

In a recent Communication to the Editor, it was mentioned[2] that Michael and Noyes[3] reaffirmed that the photoelimination of olefins from carbonyl-containing compounds, often called a type II process, occurs *via* a singlet excited state. It was felt worthwhile to report, at this time, some of the additional results obtained in our laboratory which may resolve the controversy concerning the excited state involved in the photoelimination

$$CH_3COC_3H_7{}^* \longrightarrow C_2H_4 + CH_3COCH_3 \qquad (I)$$
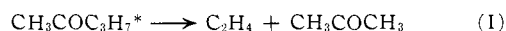
We confirm the findings of Michael and Noyes[3] that at 3130 Å., addition of biacetyl to 2-pentanone quenches

(1) This work was supported by the U. S. Public Health Service, Department of Health, Education, and Welfare.
(2) P. Borrell, *J. Am. Chem. Soc.*, **86**, 3156 (1964).
(3) J. L. Michael and W. A. Noyes, Jr., *ibid.*, **85**, 1027 (1963).

process I. In addition, it was noted that the related process[4]

$$CH_3COC_3H_7{}^* \longrightarrow CH_3C(OH)CH_2$$
$$\underset{CH_2-CH_2}{|\quad\quad|}$$
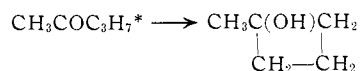
is also quenched by biacetyl. The emission measurements which were carried out in our laboratory indicate that, as noted by Michael and Noyes, a strong phosphorescence emission appears when biacetyl is added to 2-pentanone. However, the fluorescence emission from 2-pentanone, which has a maximum between 4100 and 4300 Å. (as measured on a Hilger F/4) and which is unaffected by the addition of oxygen up to 490 mm. does not vary by more than 2%. This conclusion is based on the observation that the light emitted by various 2-pentanone–biacetyl mixtures (total pressure of 30 mm.) containing 1 mm. of oxygen is identical with that emitted by pure 2-pentanone. Thus, one is forced to conclude that only triplet excited biacetyl is formed in the energy transfer process in the photolysis of 2-pentanone at 3130 Å., and that consequently process I occurs *via* a triplet excited state.

$$CH_3COC_3H_7{}^* + B \longrightarrow CH_3COC_3H_7 + B^3$$
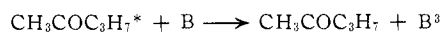
In a similar way, by measuring the emission of acetone–biacetyl, 2-butanone–biacetyl, and 3-methyl-2-butanone–biacetyl mixtures, both in the presence and in the absence of oxygen, we concluded that, as already noted for acetone,[5] only the ketone molecule excited to the triplet state transfers its energy to biacetyl. The relative efficiency of the energy transfer, which is apparently strongly dependent on the dissociative lifetime of the excited ketone molecule, was found to vary according to the sequence: acetone > 2-butanone > 2-pentanone > 3-methyl-2-butanone.

Additional data, which will be reported in the near future, also indicate that because of the efficient vibrational deactivation of the excited state at higher densities, the photoelimination from 2-pentanone and 2-hexanone, as well as the formation of the cyclic alcohols, can be quenched by biacetyl more readily in the liquid phase than in the gas phase. The quenching efficiency in the liquid phase is independent of wave length from

(4) P. Ausloos and R. E. Rebbert, *J. Am. Chem. Soc.*, **83**, 4897 (1961).
(5) J. Heicklen and W. A. Noyes, Jr., *ibid.*, **81**, 3858 (1959).

2537 to 3130 Å. but is strongly dependent on the temperature which determines the dissociative lifetime of the excited ketone molecule.

It may be noted that, in the study of Borkowski and Ausloos,[6] as in the case of the ketones, the fluorescence emitted by *n*-butyraldehyde is not quenched by the addition of biacetyl, clearly showing that a triplet state is involved. The latter conclusion is corroborated even more conclusively by a recent study[7] on the photolysis of acetone–aldehyde mixtures in which it is shown that at 3130 Å. the emission from the triplet state of acetone is quenched by *n*-butyraldehyde and that there is a corresponding photosensitization of the elimination of ethylene from *n*-butyraldehyde. It should be pointed out that from the results concerning the benzophenone-sensitized decomposition of the aldehydes recently reported,[2] no firm conclusions can be drawn unless quantum yields are determined. Chain reactions involving the abstraction of the hydrogen from the acyl group of the aldehyde, which should be intensity dependent, may lead to an apparent low olefin yield.

In the case of the benzophenone–ketone mixtures referred to by Borrell, it has not been established that energy transfer from benzophenone to the ketone occurs. Actually, energy transfer to the ketone may be endothermic[8] with the resulting effect that photoreduction of the benzophenone may become of importance.

It is clear that a generalization such as the one made recently[2] is not warranted. As noted before,[6] it is quite possible that, although at 3130 and 3340 Å. photoelimination of olefins can occur from a triplet state, at wave lengths shorter than the ones used in the investigations reported here, the same process may conceivably occur from a singlet excited state as well. Also, the probability that at any given wave length the same process will occur from either a triplet or a singlet state may depend on the structure of the compound under consideration.

(6) R. P. Borkowski and P. Ausloos, *ibid.*, **84**, 4044 (1962).
(7) R. E. Rebbert and P. Ausloos, *ibid.*, in press.
(8) G. S. Hammond, N. J. Turro, and P. A. Leermakers, *J. Phys. Chem.*, **66**, 1144 (1962).

NATIONAL BUREAU OF STANDARDS   P. AUSLOOS
WASHINGTON, D. C. 20234   R. E. REBBERT

RECEIVED AUGUST 26, 1964

BOOK REVIEWS

Fast Reactions in Solution. By E. F. CALDIN. John Wiley and Sons, Inc., 605 Third Ave., New York 16, N. Y. 1964. 306 pp. 14 × 22 cm. Price, $7.50.

This book contains a much needed and very interesting compendium of the various methods that have been used to study reactions from a range of seconds to microseconds. It also includes, as well, a chapter on the "general topics" which is interesting and useful although not closely related to the instrumental theme of the book. The book is replete with examples of the application of rapid reaction techniques to various chemical and biochemical reactions. It is well filled with references from which the reader may draw to obtain a more penetrating evaluation.

If one is to find a fault, it would be mostly in the depth of discussion of particular methods, but, of course, not much depth can be expected of a 300-page compendium which attempts to cover all methods. Nevertheless, a few examples are useful. The mixing chamber illustrated on page 31 is excellent for the rather low flow velocities for which it was designed, but fails seriously when cavitation of the flow stream must be considered. The fact that cavitation provides a limit to the time range of flow apparatuses, should have been discussed.

Another omission is in the biological applications of the flash methods; while strongly influenced by the excellent flash photolysis studies of Gibson, the author seems to have omitted only a description of the flash work of H. T. Witt, and flash studies of visual pigments merit only a small paragraph.