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

$$C—^-$$

form, $O=C—C=F^+$, 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
                RECEIVED JULY 11, 1964

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
   RECEIVED AUGUST 12, 1964

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

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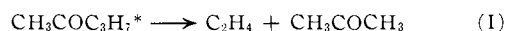
We confirm the findings of Michael and Noyes[3] that at 3130 Å., addition of biacetyl to 2-pentanone quenches

(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).