

3-Butyn-1-ol was converted into the tosylate, n^{20D} 1.5335, in 80% yield by the usual pyridine procedure. The tosylate, 100 mmol, was hydroborated in the usual manner with 200 mmol of 9-BBN and the solution was allowed to stir for 3 hr at 25°. Then 200 mmol of 1.7 M methyllithium in ethyl ether was added dropwise over 30 min and the solution was allowed to stir for 6 hr. Water, 25 ml, was added, the solution was treated with potassium carbonate, and the organic phase was separated, dried over magnesium sulfate, and distilled. There was obtained 12.6 g (65% yield) of B-cyclobutyl-9-borabicyclo[3.3.1]nonane, bp 113° (10 mm), and 10.2 g (60% yield) of B-methyl-9-BBN, bp 57° (10 mm). (All operations were carried out under nitrogen.) Oxidation of a sample of the B-cyclobutyl-9-BBN yielded *cis*-cyclooctane-1,5-diol, mp 72–73°, and cyclobutanol, bp 123–125°, n^{20D} 1.4337, pmr spectrum identical with the published spectrum.¹⁰

For the synthesis of cyclobutanol, the oxidation of the intermediate was carried out *in situ*, without isolation, utilizing aqueous sodium hydroxide, 66 ml of 3 M, and 30% hydrogen peroxide, 66 ml. Distillation yielded 4.7 g (65% yield) of cyclobutanol, bp 120–123°, n^{20D} 1.4305, pmr spectrum identical with that published.¹⁰

At the present time we are unable to account for the very great difference in the case of closure of the simple hydroboration products of 3-butenyl chloride⁴ and tosylate⁵ and the present dihydroborated intermediate. Possibly, in the present case, the dissociation of the initial addition compound (eq 7) into the carbanion¹¹ (eq 8) is greatly stabilized by the possibility of resonance with the second 9-BBN moiety, so that the relatively unfavorable displacement involved in the formation of a four-membered ring can occur.

This opens up the door to a major new route to substituted cyclopropyl- and cyclobutylboron intermedi-

ates and to the numerous derivatives into which such boron compounds can be converted.

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Herbert C. Brown, Stanley P. Rhodes¹²

Richard B. Wetherill Laboratory
Purdue University, Lafayette, Indiana 47907

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The Heat of Formation of the Methoxycarbonyl Ion

Sir:

The stabilization energy of cations has been the subject of a number of previous investigations.^{1–4} Of particular interest is the substituted methyl cation,⁴ CH_2X^+ , in which the substituents caused very large changes in the stabilization energy of the cation. These changes appear to be due to π -bond interactions between the substituent and the vacant 2p orbital on the carbon bearing the formal charge.⁴ As might be expected, the stabilization energy (SE) for $\text{X} = \text{OCH}_3$, relative to the CH_3^+ ion as zero, is greater than the SE value for $\text{X} = \text{CH}_3$ due to the formation of stable ionic structures such as $\text{CH}_3\text{O}^+=\text{CH}_2$.

The stabilization energies of the substituted cations XCO^+ appear to be markedly different from the methyl cations. Recent X-ray data and molecular orbital calculations on the acetyl ion⁵ indicate a shortened C–C bond and net positive charge on the carbonyl carbon. Thus both $\text{CH}_3\text{C}^+=\text{O}$ and $\text{CH}_3\text{C}\equiv\text{O}^+$ are likely representations of the acetyl ion. If a similar net positive charge resides on the carbonyl carbon of the methoxycarbonyl ion then unshared pair donor substituents should cause a marked stabilization of the XCO^+ ion.

(1) A. Brickstock and J. A. Pople, *Trans. Faraday Soc.*, **50**, 901 (1954).

(2) J. Halpern, *J. Chem. Phys.*, **20**, 744 (1952).

(3) A. G. Harrison and F. P. Lossing, *J. Amer. Chem. Soc.*, **82**, 1052 (1960).

(4) R. W. Taft, R. H. Martin, and F. W. Lampe, *ibid.*, **87**, 2490 (1965).

(5) F. P. Boer, *ibid.*, **88**, 1572 (1966).

(10) M. C. Caserio, W. H. Graham, and J. D. Roberts, *Tetrahedron*, **16**, 171 (1960).

(11) Compare G. Zweifel and H. Arzoumanian, *Tetrahedron Letters*, 2535 (1966), and G. Cainelli, G. D. Bello, and G. Zubiani, *ibid.*, 4315 (1966).

Table I. Energetics of the Process $\text{RCOOCH}_3 + e \rightarrow \text{CH}_3\text{OCO}^+ + \text{R} + 2e$

R	$\Delta H_f(\text{RCOOCH}_3)^a$ kcal/mol	$\Delta H_f(\text{R})^b$ kcal/mole	AP, eV	$\Delta H_f(\text{CH}_3\text{OCO}^+)$, kcal/mol
CH ₃	-97.9 ^c	34	12.60 ± 0.07 (8)	158.7
			12.31 (9)	152.0
			12.3 (10)	151.8
			12.35 ± 0.03	152.9
CH ₃ O	-143.3	2	12.15 ± 0.08	134.9
NCCH ₂	-65.2	55	11.72 ± 0.03	150.1
ClCH ₂	-103.4	28.7 ^d	11.50 ± 0.05	133.1
Cl	-103.9	28.9	11.78 ± 0.05	138.8

^a Unless otherwise indicated, values calculated by group contribution method (J. D. Cox, *Tetrahedron*, **18**, 1337 (1962)) using $\text{C}_{\text{co}} \approx \text{Cl} = -24.5$ kcal/mol and $\text{C}_{\text{co}} \approx \text{O} = -42.0$ kcal/mol. ^b Unless otherwise indicated all values taken from J. A. Kerr, *Chem. Rev.*, **66**, 465 (1966). ^c Ref 7. ^d J. C. Hassler and D. W. Setser, *J. Chem. Phys.*, **45**, 3246 (1966).

Table II. Stabilization Energies

Ion	SE, kcal/mol	Ion	SE, kcal/mol	Ion	$\Delta \text{SE}(\text{HOCH}_3)$, kcal/mol
HCH ₂	0	HCO	0	CH ₃	66
CH ₃ CH ₂	36	CH ₃ CO	40	HCO	6
CH ₃ OCH ₂	66 ^a	CH ₃ OCO	6	H ₃ COCH ₃	19
(CH ₃ O) ₂ CH	85 ^a			HC(OCH ₃) ₂	5
(CH ₃ O) ₃ C	90 ^a				

^a R. H. Martin, F. W. Lampe, and R. W. Taft, *J. Amer. Chem. Soc.*, **88**, 1353 (1966).

The stabilization energy of an ion relative to HCO^+ may be calculated by eq 1 where $\Delta H_f(\text{HCO}^+) = 198$

$$\begin{aligned} \text{SE}(\text{XCO}^+) &= [\Delta H_f(\text{HCO}^+) - \Delta H_f(\text{XCO}^+)] - \\ & \quad [\Delta H_f(\text{HCOH}) - \Delta H_f(\text{XCOH})] \\ &= 225.7 - \Delta H_f(\text{XCO}^+) + \Delta H_f(\text{XCOH}) \dots \end{aligned} \quad (1)$$

kcal/mol⁶ and the heat of formation of formaldehyde is taken as -27.7 kcal/mol.⁷ Literature values⁸⁻¹⁰ for the heat of formation of CH_3OCO^+ average about 154 kcal/mol. The heat of formation of the acetyl ion is 146 kcal/mol.^{6,11,12} Combining these values with the appropriate molecule heats of formation results in $\text{SE}(\text{CH}_3\text{CO}^+) = 40$ kcal/mol⁻¹ and $\text{SE}(\text{CH}_3\text{OCO}^+) = -11.9$ kcal/mol⁻¹, a result opposite to that expected on the basis of resonance stabilization by the methoxy substituent.

The heat of formation of the CH_3OCO ion, on which the above calculation is based, is open to question since the value is derived from appearance potential measurements only from methyl acetate. Accordingly we have redetermined the ionic heat of formation by measurement of the appearance potentials of the m/e 59 ion from a number of molecules. The results are summarized in Table I.

The ionization efficiency curves were obtained with an MS-12 mass spectrometer using an electron current of 5 or 10 μA and a repeller setting of 2-3 V. Xenon was used to calibrate the energy scale and the onset potentials were obtained using the semilogarithmic

method¹³ with readings taken down to 0.01% of the 50-V value. The present $\text{AP}(\text{CH}_3\text{OCO}^+)$ from methyl acetate is in good agreement with the values obtained by previous workers. However, the ionic heat of formation is some 20 kcal/mol greater than the lowest value recorded in Table I. It is well recognized that appearance potentials lead at best only to upper limits for the heats of formation of ions and radicals. Due to the possibility of excess energy being involved in dissociative ionization processes, some values for the appearance potentials may be quite high. Thus the lowest experimental ionic heat of formation is the best approximation to the true value. The three lowest values are in agreement, within the usual limits of error of such measurements, and lead to a value of $\Delta H_f(\text{CH}_3\text{OCO}^+) = 136 \pm 3$ kcal/mol. There is, however, no guarantee that these lowest values refer to ions in their ground state as the compounds may dissociate with the involvement of approximately equal amounts of excess kinetic energy.

A reevaluation of the stabilization energy of the methoxycarbonyl ion leads to a value of $\text{SE}(\text{CH}_3\text{OCO}^+) = 6$ kcal/mol, still substantially less than the value for the acetyl ion. To have $\text{SE}(\text{CH}_3\text{OCO}^+) \geq \text{SE}(\text{CH}_3\text{CO}^+)$ requires an involvement of about 34 kcal/mol of excess energy in the ionization processes leading to the average value of 136 kcal/mol. For methyl acetate the excess energy involved would be 54 kcal/mol, an impossibly high value for such a simple process. The amounts of excess energy involved are likely to be less than 10 kcal/mol. The SE values for the pertinent cations are given in Table II. For the methoxy substituent, two opposing effects occur, conjugative stabilization by donation of the oxygen lone-pair electrons into an adjacent vacant p orbital, and destabilization by inductive withdrawal of electrons from the adjacent atom. Assuming that the inductive effects of the methoxy substituent are approximately the same for

(6) J. L. Franklin, private communication.

(7) D. R. Stull, E. F. Westrum Jr., and G. C. Sinke, "The Chemical Thermodynamics of Organic Compounds," John Wiley & Sons, Inc., New York, N. Y., 1969.

(8) C. E. Brion and W. J. Dunning, *Trans. Faraday Soc.*, **59**, 647 (1962).

(9) S. S. Friedland and R. E. Strakna, *J. Physik. Chem.*, **60**, 815 (1956).

(10) A. B. King and F. A. Long, *J. Chem. Phys.*, **29**, 374 (1958).

(11) E. Murad and M. G. Inghram, *ibid.*, **40**, 3263 (1964).

(12) F. Doorman, *ibid.*, **42**, 65 (1965).

(13) F. P. Lossing, A. W. Tickner, and W. A. Bryce, *ibid.*, **19**, 1254 (1951).

both XCO^+ and XCH_2^+ , the difference between the methoxymethyl and methoxycarbonyl ions indicates a decreased resonance stabilization of about 60 kcal/mol in the carbonyl ion. Recent evidence⁶ indicates that the methoxymethyl ion may rearrange to the hydroxy carbonyl structure at the appearance potential threshold. The best estimate of the heat of formation of the methoxymethyl ion is however still approximately 170 kcal/mol, corresponding to an SE value of 66 kcal/mol. The increased inductive stabilization of the acetyl ion relative to the ethyl ion does provide evidence for enhanced inductive effects in the carbonyl ions so that the reduced resonance stabilization of the methoxy substituent is probably less than 60 kcal/mol.

Columns 5 and 6 of Table II illustrate the change of the stabilization energy if a hydrogen on the ion is replaced by a methoxy group. It appears that the HCO^+ ion is very similar to the $\text{H}^+\text{C}(\text{OCH}_3)_2$ ion in its stabilization effects. For the dimethoxy methyl ion both methoxy groups can compete for the charge ($\text{CH}_3^+\text{O}=\text{CHOCH}_3 \rightleftharpoons \text{CH}_3\text{OCH}=\text{OCH}_3$), thus reducing the effect of conjugation of a further methoxy group with a vacant p orbital on the carbon. Therefore it is likely that in the XCO^+ ions the oxygen atom bears the positive charge, thereby increasing the electron density on the carbonyl carbon and reducing the effect of resonance stabilization.

P. R. Briggs, T. W. Shannon
The Dow Chemical Company
Eastern Research Laboratory
Wayland, Massachusetts 01778
Received March 15, 1969

A Ketene Intermediate in the Photochemical Solvolysis of Dihydrocoumarin¹

Sir:

The photochemical solvolysis of dihydrocoumarin (**1**)² has received considerable attention. Conflicting opinions concerning the mechanism of this solvolysis have been presented by Plank³ and by Gutsche and Oude-Alink.⁴ Plank studied the photochemical hydrolysis in dioxane and deuterium oxide and concluded on the basis of deuterium incorporation (46.5% d_1 , 23.6% d_2)⁵ that the reaction proceeded *via* a ketene intermediate (**2**).³ The photochemical conversion of **1** to **2** would be strictly analogous to processes well documented in the photochemistry of cyclic ketones.⁶

Gutsche and Oude-Alink studied the reaction in methanol and methanol-*O-d* and observed no deuterium incorporation. On this basis they concluded that a ketene intermediate was not involved in the reaction and suggested an interesting spirodienone intermediate (**3**).⁴ The formation of the spirodienone is plausible in view of other photo-Fries rearrangements.

(1) Photochemical Transformations. XXXIII.

(2) J. C. Anderson and C. B. Reese, *J. Chem. Soc.*, 1781 (1963).

(3) D. A. Plank, Ph.D. Thesis, Purdue University, 1966.

(4) C. D. Gutsche and B. A. M. Oude-Alink, *J. Amer. Chem. Soc.*, **90**, 5855 (1968).

(5) Plank³ attributed the production of d_2 species to thermal recyclozation of the product to dihydrocoumarin followed by a second photochemical cleavage to the ketene and incorporation of a second deuterium.

(6) R. Srinivasan, *Advan. Photochem.*, **1**, 83 (1964).

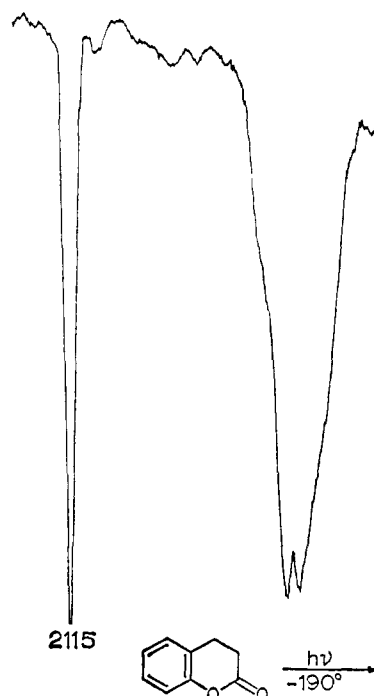
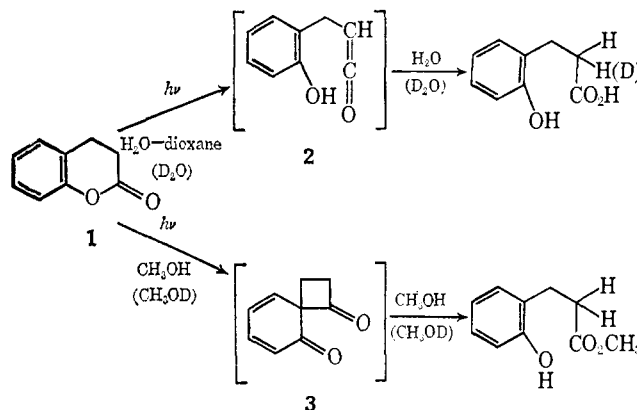


Figure 1. Infrared spectrum of 3,4-dihydrocoumarin after irradiation as a film at -190° . The new band at 2115 cm^{-1} is due to the ketene.

Our low-temperature methods⁷ seemed ideal for detecting either or both intermediates.



Irradiation of dihydrocoumarin at -190° as a thin film or as a glass containing methanol in a liquid nitrogen-cooled infrared cell using previously described techniques⁷ gave a product with a strong ketene band at 2115 cm^{-1} (see Figure 1). No new bands which could be attributed to spirodienone **3** were observed. Warming the methanol-containing glasses above -70° caused concurrent disappearance of the 2115-cm^{-1} band and appearance of the 1737- and 1716-cm^{-1} bands of methyl 3-(*o*-hydroxyphenyl)propionate. The ketene mechanism suggested by Plank is clearly operating under these conditions. In order to determine the significance of this mechanism at room temperature, we reinvestigated the deuterium-labeling experiments in deuterium oxide and methanol-*O-d*. Irradiation of dihydrocoumarin in deuterium oxide-dioxane gave 3-(*o*-hydroxyphenyl)propionic acid 52.0% d_1 and 5.5% d_2 and in methanol-

(7) O. L. Chapman and J. D. Lassila, *J. Amer. Chem. Soc.*, **90**, 2449 (1968); L. L. Barber, O. L. Chapman, and J. D. Lassila, *ibid.*, **90**, 5933 (1968); **91**, 531 (1969).