Figure 12. The π-electron density distribution in the ground (S_0) and excited singlet (S_1) states of lumichrome calculated by the SCF MO CI PPP method and the ground orbital model for methyl groups.
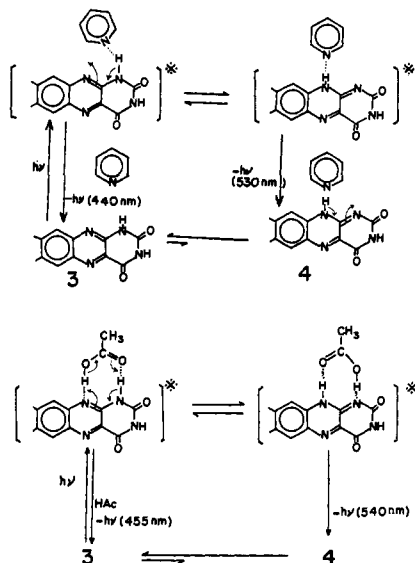

Figure 13. Possible mechanisms for the phototautomerism between lumichrome (**3**) and 7,8-dimethylisoalloxazine (**4**) catalyzed by pyridine and acetic acid. The emission maxima are indicated by "$-h\nu$".

(a) N_1-methylalloxazines do not show band II, and (b) the fluorescence spectra of isoalloxazines coincide with the band II spectra. In addition, even when band II is not clearly resolved due to viscosity and water in which resolution of the two-band system is less than that in dioxane, the enhancement in polarization degree of the band II region is characteristic of the emission from the isoalloxazine chromophore.

There was no observable solvent (D_2O) isotope effects on the phototautomeric equilibria in dioxane–pyridine and ethanol–acetic acid mixtures, when the N_1 proton was allowed to exchange with a deuteron in D_2O prior to the fluorescence measurement. Lack of the solvent isotope effect is expected for the proposed phototautomerism, particularly because $\Delta H^{\circ *}$ is practically zero and the N_1 proton (or deuteron) is merely transferred to N_{10}. The following energy level diagrams summarize the phototautomerism proposed on the basis of the present work. Similar diagrams can be constructed for alloxazine.
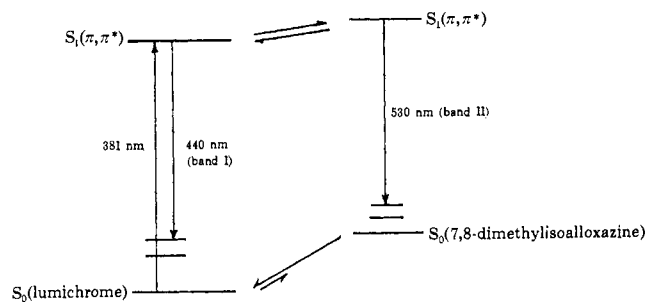
In conclusion, the significance of the present work is twofold. First, the system described can serve as a simple model for a dye laser. Second, it is possible to estimate thermodynamic data for the ground states of flavine tautomers, which are not readily obtainable in other ways.
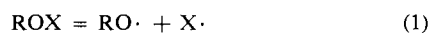
Communications to the Editor

Thermochemistry of Aliphatic Alcohols Determined by Gas-Phase Ionic Equilibria

Sir:

A number of methods have been used to determine the thermochemical properties of aliphatic alcohols. Gas kinetic methods have been applied to the pyrolysis of compounds of the type ROX where X = OR, NO,

$$ROX = RO\cdot + X\cdot \qquad (1)$$

or NO_2.[1–5] Assuming zero activation energy for the

(1) P. Gray and A. Williams, *Chem. Rev.*, **59**, 239 (1959).
(2) S. W. Benson, *J. Chem. Educ.*, **42**, 502 (1965).
(3) J. A. Kerr, *Chem. Rev.*, **66**, 465 (1966).
(4) P. Gray, R. Shaw, and J. C. J. Thynne, *Progr. React. Kinet.*, **4**, 63 (1967).
(5) S. W. Benson and R. Shaw, *Advan. Chem. Ser.*, No. 75, 288 (1968).

recombination reaction between $RO\cdot$ and $X\cdot$, ΔE for reaction 1 may be set equal to the activation energy for the decomposition reaction. The heat of formation of alkoxy radicals, $\Delta H_f^{\circ}(RO\cdot)$, can then be calculated if $\Delta H_f^{\circ}(X\cdot)$ and $\Delta H_f^{\circ}(ROX)$ are known. Electron impact mass spectrometric methods have been used to measure appearance potentials for processes such as[6,7]

$$ROX + e^- = X^+ + RO\cdot + 2e^- \qquad (2)$$
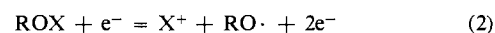
Assuming $RO\cdot$ is an alkoxy radical and not a rearrangement product, it follows that $\Delta H_f^{\circ}(RO\cdot)$ can be calculated from the measured appearance potential, $\Delta H_f^{\circ}(ROX)$, and $\Delta H_f^{\circ}(X^+)$.

(6) J. M. Williams and W. H. Hamill, *J. Chem. Phys.*, **49**, 4467 (1968).
(7) M. A. Haney and J. L. Franklin, *Trans. Faraday Soc.*, **65**, 1794 (1969).

Table I. Equilibrium Constants at 298°K for Gas-Phase Proton-Transfer Reactions[a]
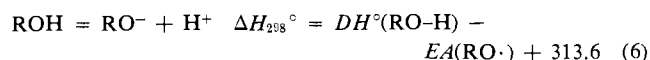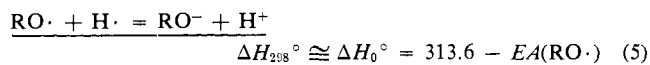
No.	B⁻ + AH = A⁻ + BH	K_{eq}	$\Delta G_{298}°$
1	$CH_3O^- + CH_3C\equiv CH = CH_3C\equiv C^- + CH_3OH$	2.7 ± 0.8	−0.6 ± 0.2
2	$CH_3O^- + C_2H_5OH = C_2H_5O^- + CH_3OH$	23 ± 2	−1.9 ± 0.1
3	$CH_3\equiv C^- + C_3H_7C\equiv CH = C_3H_7C\equiv C^- + CH_3C\equiv CH$	10.7 ± 0.5	−1.4 ± 0.1
4	$C_2H_5O^- + C_3H_7C\equiv CH = C_3H_7C\equiv C^- + C_2H_5OH$	1.2 ± 0.1	−0.1 ± 0.05
5	$C_3H_7C\equiv C^- + (CH_3)_2CHOH = (CH_3)_2CHO^- + C_3H_7C\equiv CH$	7.5 ± 0.4	−1.2 ± 0.1
6	$C_3H_7C\equiv C^- + C_2H_2 = C_2H^- + C_3H_7C\equiv CH$	10.0 ± 0.5	−1.4 ± 0.1
7	$C_3H_7C\equiv C^- + (CH_3)_3CC\equiv CH = (CH_3)_3CC\equiv C^- + C_3H_7C\equiv CH$	4.3 ± 0.5	−0.9 ± 0.1
8	$(CH_3)_3CC\equiv C^- + (CH_3)_3COH = (CH_3)_3CO^- + (CH_3)_3CC\equiv CH$	7.0 ± 1.1	−1.2 ± 0.1
9	$(CH_3)_2CHO^- + (CH_3)_3COH = (CH_3)_3CO^- + (CH_3)_2CHOH$	3.7 ± 0.6	−0.8 ± 0.1
10	$(CH_3)_3CO^- + (CH_3)_3CCH_2OH = (CH_3)_3CCH_2O^- + (CH_3)_3COH$	8.3 ± 0.9	−1.3 ± 0.1
11	$F^- + (CH_3)_3CCH_2OH = (CH_3)_3CCH_2O^- + HF$	2.3 ± 0.3	−0.5 ± 0.1

[a] $\Delta G_{298}°$ is in kcal/mol.

We would like to report the first determinations of the heterolytic bond dissociation energies of the aliphatic alcohols

$$ROH = RO^- + H^+ \qquad (3)$$
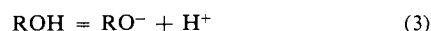
$\Delta H_{298}°$ for reaction 3 provides an independent method for calculating heats of formation of alkoxide ions and alkoxy radicals. The following thermodynamic cycle applies generally for the heterolytic bond dissociation process
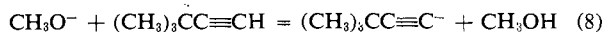
$$ROH = RO\cdot + H\cdot \qquad \Delta H_{298}° = DH°(RO-H) \qquad (4)$$

$$\underline{RO\cdot + H\cdot = RO^- + H^+}$$

$$\Delta H_{298}° \cong \Delta H_0° = 313.6 - EA(RO\cdot) \quad (5)$$

$$ROH = RO^- + H^+ \quad \Delta H_{298}° = DH°(RO-H) - $$

$$EA(RO\cdot) + 313.6 \quad (6)$$

Equation 6 shows that the bond dissociation energy can be calculated from $\Delta H_{298}°$ for reaction 3 and the electron affinity of the alkoxy radical.[8,9]

Table I shows the various gas-phase proton-transfer reactions which were studied and our results for the equilibrium constants and standard free energy changes.[10] Pulsed ion cyclotron resonance spectroscopy was utilized to measure the thermal equilibrium constants.[11-14] The pulsed icr spectrometer is essentially a mass spectrometer which is capable of trapping low energy gaseous ions efficiently for times up to several seconds. Gaseous ions are generated initially by a 10 msec pulse of an electron beam. Thermal energy electrons react rapidly with methyl nitrite to form CH_3O^- (m/e 31).

$$CH_3ONO + e^- = CH_3O^- + NO \qquad (7)$$
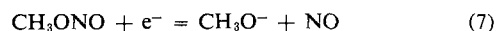
In a typical experiment (reaction 8 in Table I), CH_3O^- serves as a source of negative ions by reacting with 2,2-dimethyl-1-butyne to produce m/e 81⁻

$$CH_3O^- + (CH_3)_3CC\equiv CH = (CH_3)_3CC\equiv C^- + CH_3OH \quad (8)$$

and with tert-butyl alcohol to produce m/e 73⁻

$$CH_3O^- + (CH_3)_3COH = (CH_3)_3CO^- + CH_3OH \quad (9)$$

After a reaction period of about 300 msec an equilibrium condition is established which can be described by the reversible reaction

$$(CH_3)_3CC\equiv C^- + (CH_3)_3COH = $$

$$(CH_3)_3CO^- + (CH_3)_3CC\equiv CH \quad (10)$$

and by the equilibrium constant expression

$$K = \frac{[(CH_3)_3CO^-][(CH_3)_3CC\equiv CH]}{[(CH_3)_3CC\equiv C^-][(CH_3)_3COH]} \quad (11)$$

Numerous tests were performed to ensure that the reactions shown in Table I were being studied under conditions of thermal equilibrium.[15]

The results shown in Table I may be utilized in a number of ways. Table II can be derived by referencing

Table II. Thermochemical Data Derived from Pulsed Icr Equilibrium Studies[a]

ROH	ROH = RO⁻ + H⁺ $\Delta G_{298}°$[b]	$\Delta H_{298}°$	$\Delta H_f°(RO^-)$[c]	$DH°(RO-H)$ $- EA(RO\cdot)$
CH_3OH	370.3	376.8	−38.4	63.2 ± 0.8
C_2H_5OH	368.4	374.9	−48.5	61.3 ± 0.7
$(CH_3)_2CHOH$	367.0	373.5	−58.8	59.9 ± 0.7
$(CH_3)_3COH$	366.2	372.7	−69.2	59.1 ± 0.6
$(CH_3)_3CCH_2OH$	364.9	371.4		57.8 ± 0.6

[a] All values in kcal/mol at 298°K. [b] Calculated assuming $\Delta G_{298}° = 365.4 \pm 0.5$ kcal/mol for HF = H⁺ + F⁻. [c] Calculated using the following heats of formation, kcal/mol: $CH_3OH = -48.0$, $C_2H_5OH = -56.2$, $(CH_3)_2CHOH = -65.1$, $(CH_3)_3COH = -74.7$, and H⁺ = 367.2: D. D. Wagman, W. H. Evans, V. B. Parker, I. Halow, S. M. Bailey, and R. H. Schumm, Nat. Bur. Stand. (U.S.), Tech. Note, No. 270-3 (1968); ref 16a.

our data to a calculated value of $\Delta G_{298}°$ for the heterolytic bond dissociation of HF.

$$HF = F^- + H^+ \qquad (12)$$

Using $\Delta G_{f,298}°(HF) = -65.6$ kcal/mol, $\Delta G_{f,298}°(H^+) = 362.6$ kcal/mol, and $\Delta G_{f,298}°(F^-) = -62.8$ kcal/mol gives a value of 365.4 ± 0.5 kcal/mol for reaction 12.[16] Temperature dependence studies have not been done on these systems, so the entropy contribution to $\Delta G_{298}°$ must be estimated. We have assumed that the standard entropy of the anions RO⁻ is equal to that of the corresponding isoelectronic neutrals RF.[17] This pro-

(8) J. I. Brauman and L. K. Blair, J. Amer. Chem. Soc., 92, 5986 (1970).

(9) D. K. Bohme, R. S. Hemsworth, and H. W. Rundle, J. Chem. Phys., 59, 77 (1973).

(10) Reactions of C_2H_2 with the aliphatic alcohols in a flowing afterglow apparatus have been reported: D. K. Bohme, E. Lee-Ruff, and L. B. Young, J. Amer. Chem. Soc., 93, 4608 (1971).

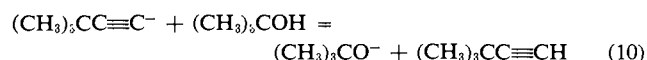(11) R. T. McIver, Jr., Rev. Sci. Instrum., 41, 555 (1970).

(12) M. T. Bowers, D. H. Aue, H. M. Webb, and R. T. McIver, Jr., J. Amer. Chem. Soc., 93, 4314 (1971).

(13) R. T. McIver, Jr., and J. R. Eyler, J. Amer. Chem. Soc., 93, 6334 (1971).

(14) R. T. McIver, Jr., and J. H. Silvers, J. Amer. Chem. Soc., 95, 8462 (1973).

(15) R. T. McIver, Jr., and J. S. Miller, manuscript in preparation.

(16) (a) D. R. Stull and H. Prophet, "JANAF Thermochemical Tables," 2nd ed, U. S. Government Printing Office, Washington, D. C., 1971. (b) $\Delta G_{f,298}°(F^-)$ has been modified to reflect the revised value for $EA(F\cdot)$ as reported by R. Milstein and R. S. Berry, J. Chem. Phys., 55, 4146 (1971).

(17) S. W. Benson, "Thermochemical Kinetics," Wiley, New York, N. Y., 1968.

cedure enables calculation of the heterolytic bond dissociation energies (column 3 of Table II) and the heats of formation of alkoxide ions (column 4 of Table II).

The differences between the O–H bond dissociation energies and the electron affinities of the alkoxy radicals (column 5 of Table II) can be calculated using eq 6. Our values for these quantities may be combined with current values for the O–H bond dissociation energies to give electron affinities of the alkoxy radicals (see Table III). Williams and Hamill have measured

Table III. Electron Affinities of Alkoxy Radicals[a]

ROH	$DH°(RO-H)$[b]	This work	Williams and Hamill[c]
		$EA(RO\cdot)$	
CH_3OH	102 ± 2	39 ± 2.8	
C_2H_5OH	102 ± 2	41 ± 2.7	39 ± 2
$(CH_3)_2CHOH$	103 ± 2	43 ± 2.7	41 ± 2
$(CH_3)_3COH$	103 ± 2	44 ± 2.6	

[a] All values in kcal/mol. [b] Reference 3. These values were assumed in our calculation of the electron affinities. [c] Reference 6.

$EA(RO\cdot)$ from the differences in the appearance potentials for processes such as

$$ROR + e^- = R^+ + RO^- + e^- \quad (13)$$

$$ROR + e^- = R^+ + RO\cdot + 2e^- \quad (14)$$
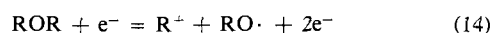
Comparison of the pulsed icr data with the appearance potential data in Table III shows surprisingly good agreement considering how different the two methods are. Recent studies indicate that the electron affinities of alkoxy radicals can be measured accurately by electron photodetachment experiments.[18] It may be possible to combine these values with our measurements of $DH°(RO-H) - EA(RO\cdot)$ to obtain more accurate values for the O–H bond dissociation energies.

Ionic equilibria studied by pulsed icr provide an independent means for calculating heterolytic bond dissociation energies and heats of formation of anions. Further studies of this type are in progress for species of known electron affinities.

(18) J. I. Brauman, private communication.
(19) Alfred P. Sloan Fellow, 1973–1975.

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Received March 5, 1974

The Thermal Conversion of Triquinacene to Azulene

Sir:

We have found triquinacene (1)[1] remarkably resistant to thermal change. The hydrocarbon survives passage

(1) (a) R. B. Woodward, T. Fukunaga, and R. C. Kelly, *J. Amer. Chem. Soc.*, 86, 3162 (1964); (b) I. T. Jacobson, *Acta Chem. Scand.*, 21, 2235 (1967); (c) H. Prinzbach and D. Stusche, *Helv. Chim. Acta*, 54, 755 (1971); (d) A. de Meijere, D. Kaufmann, and O. Schallner, *Angew. Chem.*, *Int. Ed. Engl.*, 10, 417 (1971); (e) C. Mercier, P. Soucy, W. Rosen, and P. Deslongchamps, *Syn. Commun.*, 3, 161 (1973); (f) M. J. Wyvratt and L. A. Paquette, *Tetrahedron Lett.*, in press.

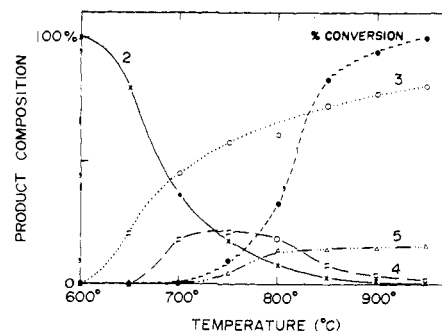Figure 1. Temperature dependence of the triquinacene pyrolysis.[2] Product compositions were determined by quantitative glc, with appropriate detector response corrections; a good material balance was observed.

through a quartz flow system[2] heated to 500° and remains incompletely consumed even at 900°. Such a degree of thermal stability exceeds that of all other known $(CH)_{10}$ compounds,[3] which now number greater than 20, and signifies that triquinacene must lie in an exceptionally deep well on the $(CH)_{10}$ energy surface.

At 600° triquinacene undergoes a clean transformation to azulene (2, low conversion).[4] This blue hydrocarbon has not previously been reported among the pyrolysis products of any $(CH)_{10}$ isomer[3] and requires the loss of two hydrogen atoms from 1, possibly as molecular hydrogen. The thermal conversion of triquinacene to azulene thus represents the lowest energy unimolecular reaction available to 1.

At 650° naphthalene (3) accompanies the azulene. Under these conditions azulene rearranges partially to naphthalene,[5] and this isomerization could reasonably account for the formation of 3.

At 700° a third product appears which does not come from either azulene or naphthalene but must be derived from triquinacene by a competing pathway. This compound, identified as 1,2-dihydronaphthalene (4), appears only at temperatures of 700° and above and must therefore be separated from 1 by an energy barrier higher than that between triquinacene and azulene.

At 750° indene (5) is found together with 2, 3, 4, and unchanged 1 in the pyrolysate. No additional products were detected in greater than 5% yield below 950°, at which temperature triquinacene no longer survives.[6] Indene and naphthalene constitute the products of independent 1,2-dihydronaphthalene pyrolysis under these conditions. The formation of indene requires a loss of CH_2, the fate of which remains undetermined.[7] Scheme I and Figure 1 summarize these thermal transformations and their temperature dependence.

Progressively lengthening the contact time at 735°

(2) All pyrolyses were conducted in a quartz tube packed with quartz chips at atmospheric pressure using a slow stream of N_2 as carrier gas. The contact time in the hot zone was adjusted to *ca.* 0.5 sec unless otherwise indicated.
(3) L. T. Scott and M. Jones, Jr., *Chem. Rev.*, 72, 181 (1972); E. E. van Tamelen, *Accounts Chem. Res.*, 5, 186 (1972); S. Masamune and N. Darby, *ibid.*, 5, 272 (1972).
(4) All pyrolysis products were identified by comparison of their glc behavior, mass spectra, and electronic spectra with those of authentic samples.
(5) This rearrangement was first reported by E. Heilbronner, P. A. Plattner, and K. Wieland, *Experientia*, 3, 70 (1947); E. Heilbronner and K. Wieland, *Helv. Chim. Acta*, 30, 947 (1947).
(6) Above 850° a minor product is produced (*ca.* 3% yield) which has the same glc retention time as styrene.
(7) In the glc we see no significant peaks for C_{11} hydrocarbons.