and brings about destruction of the metachromatic compound is not clear. That it may not involve destruction of hydrophobic bonds was pointed out above. That it is not dielectric constant seems likely from the quantitatively similar results with ethanol and urea. While no interpretation of the curves of Figs. 1 to 4 can be offered beyond their representation of the destruction of metachromatic compounds, they offer a simple and quantitative method to measure stabilities of metachromatic compounds, and in a wider field a new technique for the study of polyanions or cationic dyes in solution.

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The Effect of Substitution on the Ionization Potentials of Free Radicals and Molecules. III. Estimation of the Ionization Potentials of Cycloalkyl Radicals and Cyclic Amines by δ_K Values

BY JOYCE J. KAUFMAN

RECEIVED APRIL 20, 1962

It has been shown previously by the author (Parts I and II) that the effect of substituent groups on ionization potentials of alkylamines (Y_3N) and alkyl free radicals (Y_3C) were almost identical. From measured photoionization potentials of amines a new set of constants, δ_K values, which quantitatively reflect changes in ionization potential with substituent groups, were derived and using these, ionization potentials of alkyl free radicals could be estimated to within the experimental error of their measurements. In the present article δ_K values obtained from linear and branched alkyl substituents are shown to be extendable to cyclic substituents in which the carbon from whence the unpaired electron was being withdrawn was itself part of the ring. Using the original δ_K values it is now possible to estimate the ionization potentials of cyclic free radicals and cyclic amines.

δ_K values, a new set of constants which quantitatively measure the effect of substitution on ionization potentials, have been previously derived by the author[1,2] from measurements on substituted amines and shown to hold true also for calculation of ionization potentials of substituted linear and branched alkyl radicals. The recently published values for the ionization potentials of cycloalkyl radicals[3] enable one to verify that δ_K values have equal validity for the estimation of the ionization potentials of cycloalkyl radicals—a fact which would not have been immediately apparent.

The symbols δ_K(or $\delta_K{}^{(1)}$), $\delta_K{}^{(2)}$, $\delta_K{}^{(3)}$ are the changes in ionization potential caused by substituting one, two or three identical groups, respectively, for H atoms (on the *same* central atom of the radical or molecule from which the electrons are being withdrawn in the ionization process). Since it has been shown that there is a saturation effect on ionization potentials, another type of δ_K value is the difference in ionization potential found by adding a second identical substituent group when a first substituent group is already present. $\delta_K{}^{(1-0)}$ (or δ_K or $\delta_K{}^{(1)}$) and $\delta_K{}^{(2-1)}$ are the differences in ionization potential between mono- and unsubstituted, and between di- and monosubstituted molecules or radicals (with identical substituent groups).

Using the method outlined in ref. 1 and the table of δ_K values contained therein, the cycloalkyl radical ionization potentials are calculated as:

Cyclopropyl: $I(\text{Me}) - \delta_K{}^{(2)}(\text{Me}) = 9.96 \text{ ev.} - 1.91 \text{ ev.} = 8.05 \text{ ev. (calcd.)}$

8.05 ± 0.1 ev. (exptl.)

Cyclobutyl:

(1) $I(\text{Me}) - \delta_K{}^{(1)}(\text{Me}) - \delta_K{}^{(2-1)}(\text{Et}) = 9.96 \text{ ev.} - 1.18 \text{ ev.} - 0.85 \text{ ev.} = 7.93 \text{ ev. (calcd.)}$

or

(2) $I(\text{Me}) - \delta_K{}^{(1)}(\text{Et}) - \delta_K{}^{(2-1)}(\text{Me}) = 9.96 \text{ ev.} - 1.29 \text{ ev.} - 0.73 \text{ ev.} = 7.94 \text{ ev. (calcd.)}$

7.88 ± 0.05 ev. (exptl.)

Cyclopentyl:

(1) $I(\text{Me}) - \delta_K{}^{(2)}(\text{Et}) = 9.96 \text{ ev.} - 2.14 \text{ ev.} = 7.82 \text{ ev. (calcd.)}$

or

(2) $I(\text{Me}) - \delta_K{}^{(1)}(\text{Me}) - \delta_K{}^{(2-1)}(\text{Pr}) = 9.96 \text{ ev.} - 1.18 \text{ ev.} - 0.94 \text{ ev.} = 7.84 \text{ ev. (calcd.)}$

7.79 ± 0.03 ev. (exptl.)

Cyclohexyl:

(1) $I(\text{Me}) - \delta_K{}^{(1)}(\text{Et}) - \delta_K{}^{(2-1)}(\text{Pr}) = 9.96 \text{ ev.} - 1.29 \text{ ev.} - 0.94 \text{ ev.} = 7.73 \text{ ev. (calcd.)}$

or

(2) $I(\text{Me}) - \delta_K{}^{(1)}(\text{Me}) - \delta_K{}^{(2-1)}(\text{Bu}) = 9.96 \text{ ev.} - 1.18 \text{ ev.} - 1.02 \text{ ev.} = 7.76 \text{ ev. (calcd.)}$

7.66 ± 0.05 ev. (exptl.)

The calculated and experimental values are in excellent agreement, better than the agreement with values calculated by much more tedious methods.[3] The best expression to use for the ionization potentials of the cycloalkyl radicals for cyclobutyl and higher members  $\overset{\overset{\text{H}}{\text{C}}}{Y_1\text{—}Y_2}$, where Y_1 and Y_2 correspond to the substituent groups R_1 and R_2 with one less hydrogen (Y_1 is preferably equal to Y_2 or else it is the closest smaller one to Y_2) is $I(\text{cycloalkyl}) = I(\text{Me}) - \delta_K{}^{(1)}(R_1) - \delta_K{}^{(2-1}$

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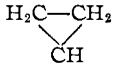
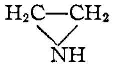
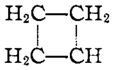
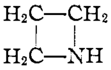
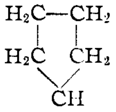
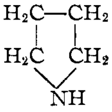
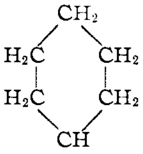
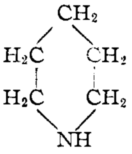
[1] Joyce J. Kaufman and W. S. Koski, *J. Am. Chem. Soc.*, **82**, 3262 (1960).

[2] Joyce J. Kaufman and W. S. Koski, paper presented before the Section on Physical Chemistry, Structure and Reactivity of Small Molecular Species, 18th International Congress of Pure and Applied Chemistry, Montreal, August 1961.

[3] R. F. Pottie, A. G. Harrison and F. P. Lossing, *J. Am. Chem. Soc.*, **83**, 3204 (1961).

TABLE I

δ_K VALUES FROM CYCLOALKYL RADICALS AND CALCULATED IONIZATION POTENTIALS OF CORRESPONDING CYCLIC AMINES

Radical	δ_K(ev.)	Cyclic amine	I (amine, calcd., ev.)
	1.91		8.24
	2.08		8.07
	2.17		7.98
	2.30		7.85

(R_2) − 0.05 ev. Apparently the non-planarity of the cycloalkyl radicals and ions has only a negligible effect on the overall behavior of ionization potential with substitution.

Since the equivalence of substituent groups on ionization potentials of radicals and corresponding amines has already been proven, it should now be possible to utilize δ_K values obtained from cycloalkyl radicals to calculate the ionization potentials of cyclic saturated amines. These are shown in Table I. The experimental values eventually to be compared with the calculated ionization potentials of the cyclic amines should come from photoionization or spectroscopic measurements since there is much scatter in the measured electron photoionization or spectroscopic measurements impact values.[4]

Ionization potentials of free radicals are of importance in appearance potential studies, in electronegativity considerations, in the determination of free radicals by gas chromatography using ionization detection and in many other applications. Ionization potentials of substituted amines are of interest in connection with the theory of charge-transfer complexes and in determining relative basicities unhampered by steric effects. It now appears that the calculation of ionization potentials by the use of δ_K values has a general validity even beyond that assumed in the original article and should enable one to estimate many values, necessary for experimental planning and theoretical interpretation, that have not yet been measured experimentally.

Acknowledgment.—The author should like to thank Dr. F. P. Lossing for graciously sending information on experimentally measured ionization potentials in advance of publication.

(4) R. W. Kiser, "Tables of Ionization Potentials," TID-6142 U.S. A.E.C., June 20, 1960.

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Photochemical Oxidations. I. Ethyl Iodide

BY JULIAN HEICKLEN AND HAROLD S. JOHNSTON

RECEIVED JULY 9, 1962

The room temperature (25 ± 2°) photo-oxidation of ethyl iodide (0.06 to 2.8 mm.) in oxygen (2.8 mm.) with continuous ultraviolet radiation (usually above 2200 Å.) has been studied by irradiation in a cylindrical volume with a pinhole leak directly into a Bendix model 14 time-of-flight mass spectrometer. The initial products observed are C_2H_5OH, CH_3CHO, and I_2 in large amounts and $C_2H_5OOC_2H_5$, C_2H_5OOH, and C_2H_5OI in small amounts. Because of the cracking pattern of the reactants, it was impossible to establish the presence or absence of CH_4, C_2H_2, C_2H_4, C_2H_6, $HCHO_2$, CO_2 and HI. From mass balance HI was inferred to be a minor initial product. A fairly satisfactory nine-step mechanism can be found for the initial rate data, and several ratios of rate constants were evaluated from the data. The reaction was studied to about three per cent. completion, at which point diffusion of products through the pin-hole balanced the rate of photochemical production. The rate of attainment of this steady state and the steady-state pressures gave additional information beyond that found for the initial rates. The reaction at a few per cent. conversion of ethyl iodide is much more complex than the initial reaction: there is secondary production of alcohol, strong secondary destruction (perhaps largely heterogeneous) of C_2H_5OOH and C_2H_5OI, and slight over-all inhibition by I_2. Water was observed as a secondary product, coming in after a pronounced induction period. Even with a 14-step mechanism, all features of the reaction at three per cent. completion could not be explained. Although considerable effort was directed toward finding ozone in this system, it was never present in an amount as great as 10^{-8} atm.

Introduction

The photo-oxidation of methyl iodide has been studied extensively.[1-4] In recent years there has been agreement that the primary photochemical act is dissociation of the iodide

$$RI + h\nu \longrightarrow R + I \qquad (a)$$

in the presence of oxygen the radical forms the

$$R + O_2 + M \longrightarrow RO_2 + M \qquad (b)$$

peroxy radical, iodine atoms associate to form mo-

$$I + I + M \longrightarrow I_2 + M \qquad (c)$$

lecular iodine, and the molecular iodine formed provides competition[4] with the oxygen for the alkyl radical

$$R + I_2 \longrightarrow RI + I \qquad (d)$$

For methyl radicals Christie[4] found the ratio of rate constants, k_b/k_d, to be 5.4 × 10^3 cc./mole and 5.4 × 10^2 cc./mole when M is CH_3I and CO_2, respectively.

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(1) J. R. Bates and R. Spence, *J. Am. Chem. Soc.*, **53**, 1089 (1931); J. R. Bates and R. Spence, *Trans. Faraday Soc.*, **27**, 468 (1931).

(2) W. J. Blaedel, R. A. Ogg, Jr., and P. A. Leighton, *J. Am. Chem. Soc.*, **64**, 2500 (1942).

(3) R. B. Martin and W. A. Noyes, Jr., *ibid.*, **75**, 4183 (1953).

(4) M. I. Christie, *Proc. Roy. Soc.* (*London*), **A244**, 411 (1958).