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appropriate carrier substances to the bromination mixture obtained when radioactive bromine of a high specific activity was used.

It seemed highly improbable that organic chemists had overlooked the formation of such large quantities of lower bromides, as claimed by Williams and Hamill, in the bromination of normal hydrocarbons. A study was therefore made of the products formed in the vapor phase bromination of *n*-pentane at 80°. Over 94 percent of the theoretically possible amount of bromine used was recovered as amyl bromides, with the rest probably swept out of the apparatus with the hydrogen bromide gas formed in the reaction. A very careful but unsuccessful search was made for low boiling alkyl bromides.

Therefore, it appears to us that the statement of these investigators,¹ "In conclusion, we wish to emphasize that the experimental evidence for considerable fragmentation of the carbon chain in photobromination of *n*-pentane at 80°C seems to us quite inescapable," must be regarded with considerable reserve by organic chemists, and that the technique which led to their erroneous conclusion should be critically examined.

¹ Williams and Hamill, *J. Am. Chem. Soc.* **72**, 1857 (1950); Hamill, Williams, and Voiland, Brookhaven Conference Report No. 4, p. 90 (1950).

Reduction Potentials and Unsaturation Energy Changes in Electrode Reactions Leading to the Formation of Acridyl Radicals

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(Received July 31, 1952)

THE occurrence of stable semiquinones as intermediates in the reduction of some phenazines has been studied in detail,¹ mainly by potentiometric methods; but although it has often been proposed that semiquinone formation occurs in reactions involving the corresponding mono-aza hydrocarbons, the acridines,² quantitative data for these systems have only recently become available.

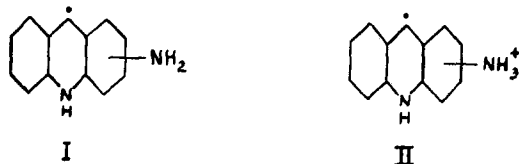


FIG. 1. Radical types considered.

The two-step reduction of a series of aminoacridines at the mercury capillary electrode has been studied by Kaye and Stonehill³ under conditions such that specific adsorption effects (complications arising from which often obscure the significance of current-potential data for systems involving semiquinones) are absent, or are at least greatly minimized. The aminoacridines, in general, reduce in two one-electron steps, both of which may be *pH*-dependent; the first step leads to the formation of radicals of types I or II (Fig. 1), depending on the acidity of the solution.

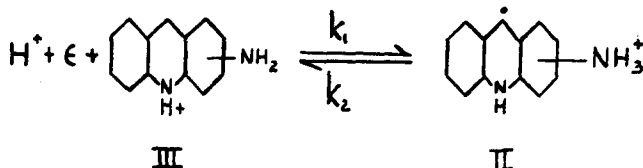
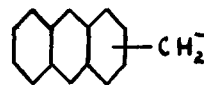


FIG. 2. Reaction of ionized aminoacridine II from radical of type II.



IV

FIG. 3. Anthracenemethyl anion, type IV.

These measurements are useful, as they constitute the only case where quantitative information on semiquinone formation is available over a range of systems of which the oxidants are conjugated molecules which are iso- π -electronic with each other. This being so, it is of interest to inquire whether there is a correlation between the observed reduction potentials and the changes in π -electron energy accompanying the electrode reaction.

In this preliminary treatment, attention is confined to the reaction in which ionized aminoacridine (III) is reduced to an ionized acridyl of type II, as in Fig. 2. Where the rates of all other reactions affecting the concentration of III and II at the electrode interface are small compared to the (composite) rates $k_1(\text{III})(\text{H}^+)$ and $k_2(\text{II})$ at potentials in the vicinity of the half-wave point, we may write,* for a series of aminoacridines,

$$F\delta V_{\frac{1}{2}} = -\delta(\Delta G_a) \approx \delta Q_a, \quad (1)$$

where $V_{\frac{1}{2}}$ is the half-wave potential, F is the Faraday, and ΔG_a and Q_a are, respectively, the free energy change and the exothermicity of the reaction in Fig. 2.

The conditions under which (1) is valid are not completely fulfilled for these systems; but, on the assumption that H^+ participates in the transition state of reaction, it may be assumed⁴ that partial irreversibility of Fig. 2 will modify the relationship

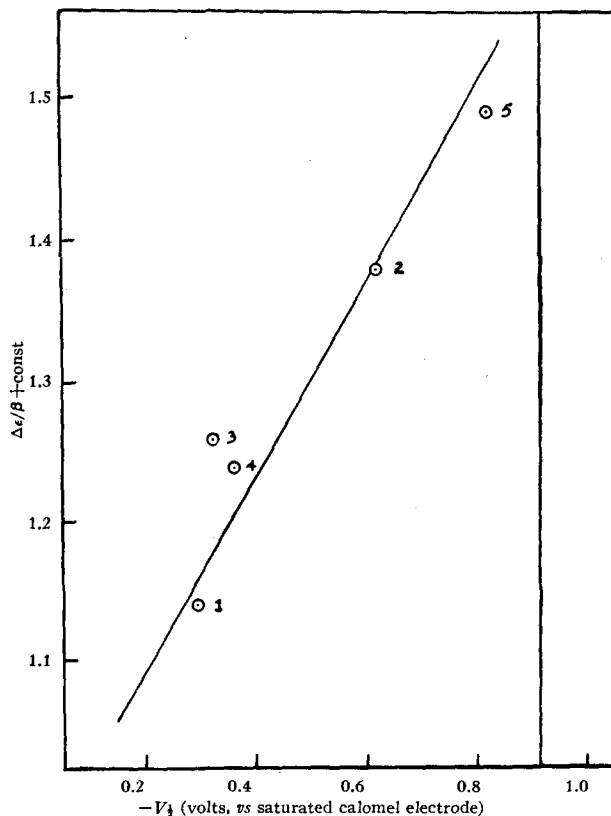


FIG. 4. Observed value of half-wave potential plotted against $\Delta\epsilon/\beta$.

between V_1 and Q_a in such a way that (1) may now be reformulated as

$$F\delta V_1 \approx \alpha(\delta Q_a) \quad (1 > \alpha > 0), \quad (2)$$

so that in either case a linear relationship between V_1 and Q_a should obtain.

Variations in $-Q_a$ for the systems we are considering can to a reasonably good approximation be equated to the change of unsaturation energy $\Delta\epsilon$ accompanying the reaction shown in Fig. 2. This may be calculated quite simply by the LCAO MO method, in combination with first-order perturbation theory.⁵ Noting that the hydrocarbon iso- π -electronic with III is an anthracenemethyl anion of type IV (see Fig. 3), while that iso- π -electronic with the acridyl II is an anthracene molecule with one electron placed in the lowest unoccupied MO, and taking into account only the effects arising from perturbations of Coulomb integrals of the hydrocarbon species on nitrogen substitution, the energy change $\Delta\epsilon$ may be expressed as

$$\Delta\epsilon = \text{const} - \epsilon_{\text{conj}} - q_1'x - q_2'y, \quad (3)$$

where III is a monoaminoacridine; in Eq. (3), ϵ_{conj} is the conjugation energy of the $-\text{CH}_2$ group to the aromatic nucleus in IV, q_1' and q_2' are the net π -electron charge densities at the position of aza-substitution and at the extracyclic atom, respectively, in IV,

x is the difference in Coulomb integral of N and carbon in the

aromatic CH grouping, and y is the corresponding difference in

Coulomb integral for $-\text{NH}_2$ and $-\text{CH}_2^-$ in the extracyclic positions. Since q_1' and q_2' are always ≥ 0 and the Coulomb terms for nitrogen are more negative than those for the carbon centers, the variable terms in (3) are all of the same sign. The terms x and y should be of comparable orders of magnitude, and for the purposes of this approximate correlation we shall assume $x = y = \beta_{\text{CC}}$, where β_{CC} is the C-C resonance integral.

From Eqs. (2), (3), and the foregoing discussion, it follows that the plot of $\Delta\epsilon/\beta$ against $-V_1$ for reactions of the type in Fig. 2 should be roughly linear, with a positive slope. The observed values of $-V_1$ (measured in fifty percent $E+\text{OH}$) are plotted against $\Delta\epsilon/\beta$, calculated according to Eq. (3),[†] in Fig. 4, and it is seen that these predictions are borne out. Although more detailed calculations are desirable, there can be little doubt that the order of reduction potentials⁵ correlates simply with the change of unsaturation energy involved in passing from ionized aminoacridine to ionized acridyl radical.

¹ L. Michaelis, Ann. N. Y. Acad. Sci., 40 (1940).

² A. Albert, *The Acridines* (Edward Arnold and Company, London, 1951).

³ R. Kaye and H. Stonehill, (a) J. Chem. Soc. 1951, 27; (b) 1951, 2638.

⁴ Differences in entropy of reduction are assumed to be small.

⁵ M. G. Evans and N. S. Hush, J. chim. phys. 49, 159 (1952).

⁶ H. C. Longuet-Higgins, J. Chem. Phys. 18, 265, 275 (1950).

⁷ C. A. Coulson and H. C. Longuet-Higgins, Proc. Roy. Soc. (London) A191, 39 (1947); 192, 16 (1947).

[†] For the 2- and 5-isomers, the values of V_1 at PHO for the reaction in Fig. 2 have been determined by extrapolation in Fig. 4 and other figures as in Table 2 of Kaye and Stonehill's paper [see reference 3(b)]. In calculating $\Delta\epsilon$, the small effect due to variation in Coulomb integral for aromatic carbon at the point of attachment of the $-\text{NH}_2^+$ group in II has been neglected.

Theory of Absorption Spectra of Carotenoids According to Tomonaga-Gas Model of π -Electrons

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(Received July 28, 1952)

AN explanation of the relation between absorption spectra and molecular structure of organic dyes was attempted by Kuhn¹ on the basis of quantum mechanics. His theoretical result

TABLE I. Absorption maxima of Carotenoids (λ is measured in $m\mu$).

Carotenoids	N	λ_{obs}	λ_{calc}	δ
Dibenzylbutadiene ^a	4	235	246	0.1078
Dibenzylhexatriene ^a	6	270	272	0.1818
Isodesmethylaxerophthene ^b	8	306	304	0.2873
Isoaxerophthene ^b	8	308	304	0.2873
Axerophthene ^c	10	346	339	0.4209
Desmethylaxerophthene ^c	10	346	339	0.4209
Isoanhydrovitamin A ^d	10	347	339	0.4209
Anhydrovitamin A ^d	12	370	370	0.5819
	14		397	0.7700
Dihydro- β -Carotene ^e	16	420	420	0.9852
	18		438	1.227
Anthraxanthin ^f	20	450	454	1.497
γ -Carotene ^g	22	462	468	1.793
Rubixanthin ^b	22	462	468	1.793
Lycopene ^a	22	472	468	1.793
Rhodoxanthin ⁱ	24	480	479	2.116
Rhodoviolascini ⁱ	26	492	489	2.466
	28		497	2.843
Dehydrolycopene ^j	30	504	504	3.247
Decapreno- β -Carotene ^k	30	508	504	3.247

^a K. W. Hausser and A. Smakula, Angew. Chem. 47, 657 (1934).

^b Karrer, Karanth, and Benz, Helv. Chim. Acta 32, 1036 (1949).

^c P. Karrer and J. Benz, Helv. Chim. Acta 31, 1607 (1948).

^d Isler, Huber, Ronco, and Kofler, Helv. Chim. Acta 30, 1911 (1947).

^e P. Karrer and A. Rügger, Helv. Chim. Acta 23, 955 (1940).

^f G. Tappi and P. Karrer, Helv. Chim. Acta 32, 50 (1949).

^g Zechmeister, Le Rosen, Schroeder, Polgar, and Pauling, J. Am. Chem. Soc. 65, 1940 (1943).

^h R. Kuhn and C. Grundmann, Ber. deut. chem. Ges. 67, 339 (1934).

ⁱ P. Karrer and E. Würzler, Helv. Chim. Acta 26, 116 (1943).

^j P. Karrer and J. Rutschmann, Helv. Chim. Acta 28, 793 (1945).

^k P. Karrer and C. H. Eugster, Helv. Chim. Acta 34, 28 (1951).

was not in good agreement with experiment. He neglected interactions between electrons. We have calculated the first excitation energy for carotenoid molecules fully taking into account the interactions, and we have been able to greatly improve the agreement of theory with experiment. A short account of our result will be given in the following:

We consider a one-dimensional longitudinal motion of N electrons in a pipe with a rectangular section. The length and sectional area of the pipe are denoted by L and A , respectively. Tomonaga² showed that this system of fermions can be considered as a system of bosons (the Tomonaga gas), and he derived a formula for energy levels of the system in terms of numbers of excited bosons and the one-dimensional potential of two-electron forces. We assume that the one-dimensional potential of Tomonaga is given by an average of the Coulomb potential, of two-electron

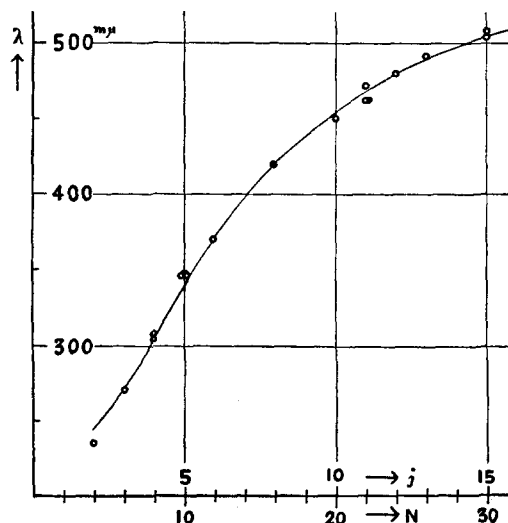


FIG. 1. Relation between absorption maxima and number π -electrons of carotenoids. λ : absorption maximum; j : number of conjugated double bonds; N : number of π -electrons; full curve: present theory; circles: observed values. (See references a-k, Table I.)