2,3-dimethoxyacridine. The bulk of the trials gave products which contained minor amounts of arsenic, and repetition failed to yield substances having constant ratios of nitrogen to arsenic content. 6-Chloro-9-(4-diethylaminobutylamino)-2-methoxyacridine (II) yielded a yellow substance which had the approximate formula $(II)\cdot 2HCl\cdot H_3AsO_3$; it contained no ionic arsenic. No structure has been formulated for either of the products containing non-ionic arsenic.

A number of unsuccessful attempts were made to prepare arsenic(III) complexes of several amines (4-diethylamino-1-methylbutylamine, 4-diethylaminobutylamine, 3-diethylamino-2-hydroxypropylamine and N-(2-hydroxyethyl)-ethylenediamine) and also certain 4-aminoquinolines (chloroquine and its 3-methyl analog, and also 7-chloro-4-[2-(2′-hydroxyethylamino)-ethylamino]-quinoline).

Experimental

Arsenic(III) Complex of 9-(3-Diethylamino-2-hydroxypropylamino)-2,3-dimethoxy-6-nitroacridine.—A solution of 1.1 g. of 9-(3-diethylamino-2-hydroxypropylamino)-2,3-dimethoxy-6-nitroacridine dihydrochloride[5] in 5 cc. of water was treated with a solution prepared by dissolving 0.2 g. of arsenic(III) oxide in aqueous sodium hydroxide (0.16 g. in 3 cc. of water). At first, a precipitate formed, then dissolved to produce a clear garnet solution. No solid separated on chilling, however the addition of *ca.* 50 cc. of dioxane caused a reddish solid to precipitate. The crude substance was crystallized twice from methanol to yield 0.7 g. of reddish-orange microcrystals, m.p. 197–199° dec. (cor.). It dissolved in water to 1% w./v.; the solution had a *p*H 6.25 and gave a precipitate at *p*H 6.30 when 0.1 *N* NaOH was added. No ionic arsenic was present in a solution of the substance.[6]

Anal. Calcd. for $3C_{22}H_{27}N_4O_5\cdot As_2O_3\cdot H_2O$: N, 11.22; As, 10.01; H_2O, 1.20. Found[7]: N, 11.16; As, 9.92, 9.99; H_2O, 1.28.

Alteration of the ratio of the acridine to arsenic over a reasonable range produced the same substance. When the original reaction mixture was diluted with water, or concentrated *in vacuo*, the base I, was obtained in most cases. It was undesirable to reflux the reaction mixtures, for otherwise the base was the only product. This latter fact does not lend much support to the possibility that ring arsenation occurs in the reaction.

Arsenic(III) Complex of 6-Chloro-9-(4-diethylaminobutylamino)-2-methoxyacridine Dihydrochloride.—Arsenic(III) oxide (0.7 g.) was dissolved in aqueous sodium hydroxide (0.61 g. in 3 cc. of water); this solution of sodium arsenite was added to 5.13 g. of 6-chloro-9-(4-diethylaminobutylamino)-2-methoxyacridine dihydrochloride trihydrate[8] in 6 cc. of water at 60°. A reddish oil separated, then a carmine solution resulted when some dioxane was added; however, dilution with dioxane to a total volume of 250 cc. gave an orange precipitate (3.9 g.). The product was crystallized twice from methanol–dioxane, from which it separated as yellow microcrystals (after drying at 100° (1 mm.) it weighed 3.2 g.), m.p. 222–223° dec. (cor., immersed at 210°). An aqueous solution failed to give a test for ionic arsenic.[6]

Anal. Calcd. for $C_{22}H_{28}ClN_3O\cdot 2HCl\cdot H_3AsO_3$: N, 7.18; Cl (ionic), 12.12; As, 12.81. Found[7]: N, 7.29; Cl (ionic), 11.70; As, 11.30.

Repetition of the experiment gave a product which melted at 226–227° dec., but contained only 9.33% arsenic.

STERLING–WINTHROP RESEARCH INSTITUTE
RENSSELAER, NEW YORK

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(5) Prepared by a method essentially as reported by C. S. Miller and C. A. Wagner, *J. Org. Chem.*, **13**, 891 (1948).

(6) As indicated by lack of uptake of iodine in usual conditions with sodium hydrogen carbonate present. The original solution of sodium arsenite responded to this test as expected.

(7) Analyses by Mr. M. E. Auerbach and staff of the Analytical Division of this Institute.

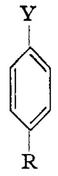
(8) W. Huber, R. K. Bair and S. C. Laskowski, THIS JOURNAL, **67**, 1619 (1945).

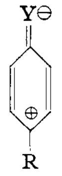
Regarding the Inherent Order of Electron Release by Alkyl Groups Attached to Electron Demanding Unsaturated Systems

BY W. A. SWEENEY AND W. M. SCHUBERT

RECEIVED MAY 17, 1954

We have evidence that the inherent *order* of electron release by alkyl attached to electron demanding unsaturated systems may not be the same as that postulated for predominant C–H hyperconjugation.[1] In Table I are values for the E-band of compounds of type I. This band results from excitation to a state in which there is a greater contribution of dipolar structures (Ia, Ib).[2] Y is electron attracting to enhance differences in electron release of *p*-alkyls.


I


Ia

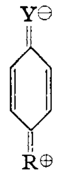

Ib

TABLE I

Compound[a]	λmax	mμ (ε)
Acetophenone	242.0	13,100
p-Methylacetophenone	253.0	14,100
p-Isopropylacetophenone	253.5	15,600
p-*t*-Butylacetophenone	253.0	16,600
Nitrobenzene	260.0	8,160
p-Methylnitrobenzene	275.0	9,400
6-Acetylindane	258.0	13,200
7-Acetyltetralin	258.5	13,400
2-Acetyltetrahydrocycloheptabenzene	258.5	14,400
2-Acetylhexahydrocyclooctabenzene	258.5	13,400
Conjugate acid of:		
Acetophenone[c]	295.5	21,500
p-*t*-Butylnitrobenzene	275.0	9,950
Benzoic acid[b]	228.0	11,830
p-Methylbenzoic acid[b]	236.5	14,620
p-*t*-Butylbenzoic acid[b]	237.5	16,290
p-Methylacetophenone[c]	312.5	24,500
p-Isopropylacetophenone[c]	315.0	24,500
p-*t*-Butylacetophenone[c]	315.5	27,100
p-Methylnitrobenzene[d]	375.5	
p-*t*-Butylnitrobenzene[d]	380.5	

[a] All spectra in 95% ethanol except as noted. Beckman DU used. [b] Solution about 0.01 *N* in HCl. [c] Spectrum in concentrated H_2SO_4. [d] Measured in 101% H_2SO_4 in which nitro compounds are known to fully ionize to conjugate acid. Extrapolated to zero time (slow sulfonation was occurring) without an exact measure of the extinction coefficient being obtained.

The trend, both in λ_{max} and ϵ, may be opposite in *order* to the number of α-hydrogens, and the spread in λ_{max} is greatest when Y is most strongly electron demanding. Furthermore, no ring size effect in the order of steric inhibition of C–H hyperconjugation is observed.[9,10] The ionization potentials of alkylbenzenes[3] also are opposite in *order* to that expected for predominant C–H hyperconjugation, despite a large demand for electron

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(1) *Cf.* J. W. Baker, "Hyperconjugation," Oxford University Press, London, 1952.

(2) See, *e.g.*, K. Bowden and E. A. Braude, *J. Chem. Soc.*, 1068 (1952).

(3) W. C. Price, *Chem. Reviews*, **41**, 262 (1947).

release by alkyl in the excited positive ion. Other physical measurements (study, *e.g.*, ref. 1), while tending to show a definite release effect by alkyl, have not unequivocally demonstrated the C–H hyperconjugative *order* of release.[4]

We suggest that at least part of the apparent contradiction between spectral and ionization potential data and rate data (for reactions in which there is a large demand for electron release in the transition state) may be explained by steric hindrance to solvation. This effect has been invoked by C. C. Price to account for reactivity orders in the saponification of *m*- and *p*-substituted alkyl benzoates.[7a,b] Price also suggested this factor may explain the similar rates of bromination of *t*-butyl- and neopentylbenzene.[11c] In the S_N1 reaction of benzhydryl chlorides,[8] solvation of the intermediate "ion" at the partially positive sites in the neighborhood of the alkyl group would be hindered more by *t*-Bu than Me and this solvation factor should contribute to increasing E_A *and* $\Delta S^{\ddagger}$ values in the order Me < *t*-Bu (compare Table II). The rate data of Baddeley[9] can be accounted for by either steric inhibition to C–H hyperconjugation or solvation. The significant $\Delta S^{\ddagger}$ changes are consistent with the latter. Arnold's *k* data on similar systems[10] fit either explanation, but there is no clear trend in E_A and $\Delta S^{\ddagger}$. The solvation factor also could play a role in the rate differences found in the bromination of C_6H_5R[11,12] and $C_6H_5CH_2R$.[11]

TABLE II

HYDROLYSIS OF *p*-$RC_6H_4CHCl\phi$ IN 80% AQUEOUS ACETONE[8]

R =	H	Me	Et	*i*-Pr	*t*-Bu
$10^6 k_1$ (0°)	2.82	83.5	62.6	46.95	35.9
E_A (kcal.)	21.0	18.9	19.4	19.8	20.05
$\Delta S^{\mp}$	−8.9	−9.8	−8.6	−7.7	−5.6

In light absorption, excitation occurs too rapidly to allow reorientation of solvent molecules.[13] Solvation of the ground state of the neutral molecules of Table I should be important only around the functional group and hence play a very minor role in determining differences in excitation energy. In the conjugate acids, appreciable positive charge is relayed to the ring, hence steric hindrance of solvation may contribute to the larger spread in λ_{max} values.

The evidence presented indicates other modes of interaction, particularly C–C hyperconjugation, or perhaps induction and internal dispersion forces,[14] may be more important than C–H hyperconjugation even when alkyl is attached to an electron demanding system.

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[4] Changes in the low intensity B-band spectra (excitation to homopolar forms) of alkylbenzenes attributed to a C–H hyperconjugative order of electron release (F. A. Matsen, W. W. Robertson and R. L. Chuoke, *Chem. Reviews*, **41**, 273 (1947)) have been given a different interpretation by several authors.[2,5,6]

(5) V. J. Hammond, W. C. Price, J. P. Teegan and A. D. Walsh, *Discuss. Faraday Soc.*, **9**, 53 (1950).

(6) J. R. Platt and H. B. Klevens, *Chem. Reviews*, **41**, 301 (1947).

(7) (a) C. C. Price and D. C. Lincoln, THIS JOURNAL, **73**, 5836 (1951); (b) C. C. Price and W. J. Belanger, *ibid.*, **76**, 2682 (1954).

(8) E. D. Hughes, C. K. Ingold and N. A. Taher, *J. Chem. Soc.*, 262 (1937).

(9) G. B. Baddeley and M. Gordon, *ibid.*, 2190 (1952).

(10) R. T. Arnold and W. L. Truett, THIS JOURNAL, **73**, 5508 (1951).

(11) (a) E. Berliner and F. Bondhus, *ibid.*, **68**, 2355 (1946); (b) E. Berliner and F. Berliner, *ibid.*, **71**, 1195 (1949); (c) E. Berliner and F. Berliner, *ibid.*, **72**, 222 (1950).

(12) P. D. B. de la Mare and P. W. Robertson, *J. Chem. Soc.*, 279 (1943).

(13) This assumption is involved in the commonly invoked Franck–Condon principle; see, *e.g.*, N. S. Bayliss, *J. Chem. Phys.*, **18**, 292 (1950).

(14) W. T. Simpson, THIS JOURNAL, **73** 5363 (1951).

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF WASHINGTON
SEATTLE 5, WASHINGTON

[CONTRIBUTION FROM COTTON FIBER SECTION, U. S. DEPT. OF AGRICULTURE, SOUTHERN REGIONAL RESEARCH LABORATORY[1]]

The Effect of Aqueous Hydrochloric Acid on the Cotton Cellulose III Lattice and Its Implications Concerning the Determinations of Crystallinity and Leveling-off Degree of Polymerization[2]

BY LEON SEGAL AND MARY L. NELSON

RECEIVED MARCH 1, 1954

Cotton cellulose III, prepared by treating cotton in anhydrous ethylamine and decomposing the resulting amine–cellulose complex by removing the amine by evaporation, was subjected to the action of hydochloric acid of various concentrations at high and low temperatures. X-Ray diffraction patterns of the resulting hydrocelluloses showed that reversion of cotton cellulose III to cellulose I, which takes place readily in boiling water, is almost completely prevented upon heating in acid when the concentration is 6 *N*, and takes place only to a slight and essentially equal extent in hot 4 and 2 *N* acid. Very dilute acid (0.1 *N*) does not prevent reversion. These observations indicate that two methods employing hot strong acid for evaluating fine-structure characteristics of cellulosic materials may be applied with reasonable confidence to cotton cellulose III. Some interesting results of application of hot hydrochloric acid to an experimental material containing both cellulose I and cellulose III are described.

Introduction

Davis and co-workers[3] have shown by X-ray diffraction studies that when cellulose is treated with anhydrous ethylamine, an ethylamine–cellulose addition compound is formed. Removal of the amine by evaporation causes a decomposition of the amine–cellulose complex, and as Segal and co-workers[4] have shown using cotton cellulose and ethylamine, this gives the cellulose III crystal modification. Segal and co-workers[4] found that immersion of

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(1) One of the laboratories of the Southern Utilization Research Branch, Agricultural Research Service, U. S. Department of Agriculture. Article not copyrighted.

(2) Presented at the Regional Conclave of the American Chemical Society, New Orleans, La., December 10–12, 1953.

(3) W. E. Davis, A. J. Barry, F. C. Peterson and A. J. King, THIS JOURNAL, **65**, 1294 (1943).

(4) L. Segal, L. Loeb and J. J. Creely, *J. Polymer Sci.*, **13**, 193 (1954).