

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, BROOKHAVEN NATIONAL LABORATORY, UPTON, N. Y.]

Hyperconjugation Theory of Carbonium Ion Reactions¹

BY S. EHRENSON

RECEIVED JULY 31, 1963

The notion that hyperconjugation may be the major driving force in some reactions where carbonium ion products or transition states are formed is supported by results of semiempirical LCAO-MO theory reported here. In the particular cases of aromatic and olefin protonations, good internal consistency is found among several organic chemical rules, parameters in the Taft linear free energy equation, and the theoretical energies computed for these reactions. The Baker-Nathan effect, Markownikoff, and Saytzeff-Wagner rules are rationalizable in terms of hyperconjugative models of various refinements. Analogous effects noted in the ultraviolet spectral shifts for the alkylbenzenes are discussed. The effects of inductive electron donation in these systems and the possibilities of ion stabilization by nonclassical structures are also examined.

1. Introduction

It is a matter of continuing controversy whether ascription to hyperconjugation (HCJ) of several clearly demonstrable effects accompanying alkyl substitution in organic molecules is justified.² The observables provoking disagreement in interpretation cover a broad range, *e.g.*, bond length variations, ultraviolet frequency and n.m.r. proton shifts, e.s.r. splittings, and reactivities in the vapor and solution phases. As a result of such widespread and often less than discriminate use, the concept has drawn many criticisms. These seem at times capable of impairing by generalization whatever utility HCJ might have upon careful application.

Perhaps the most detailed, useful, and, at the same time, most widely criticized application of the HCJ concept has been in explanation of the enhanced effects noted for *p*- vs. *m*-position alkyl substitution on various aromatic molecule reactivities. The criticisms naturally are directed in terms of alternative explanations³; although many are provocative, none at present seem any more satisfactory in the general sense than hyperconjugation. The latter seems quantitatively most compelling when viewed in the context of the dual substituent linear free energy equation. Taft and Lewis⁴ have shown that the inductive-resonance effect separations made for the alkyl groups as substituents are normal with respect to similar separations for groups where conjugative ability is generally accepted. Further, the Baker-Nathan effect⁵ may be rationalized in terms of a larger C-H than C-C bond contribution to σ_R . Additivity per bond, C-H and C-C, to the total effect of the particular alkyl group is also found, in agreement with empirical rules previously noted.^{2b,5}

In this paper, a semiempirical LCAO-MO investigation is described for electrophilic substitution reactions which, as a group, are well represented in the Taft correlations. Specifically considered are protonation reactions of olefinic and aromatic molecules which result in carbonium ions in the product or transition states. These ions, very different from their precursors, are expected by virtue of the isovalent HCJ interactions possible to be most favorable subjects for articulation of resonance effects on reactivities. Comparisons are sought with the applicable Taft correlation parameters. Special attention is paid to the relative C-H to C-C bond HCJ effects and their variations between aromatic

and olefinic reactivities. Coincidental questions such as the theoretical implications of the Markownikoff⁶ and Saytzeff-Wagner rules⁷ are also examined, again in the attempt to find the common ground for theory, empirical correlations, and chemical intuition.

2. Theory

Previous work where HCJ effects on the basicities of the methylbenzenes were examined⁸ provided the basis for the present study. The model employed is a refinement of the one developed in that work, to the extent where two-dimensional HCJ (*i.e.*, quasi- π_x and π_y) with Coulomb, exchange, and overlap integral coupling between dimensions is considered. A further extension allowing generation of self-consistent eigenvalues and vectors for excited states was also made. The latter was used in calculations on the ultraviolet frequency shifts accompanying the alkylation of benzene.

The Wheland model,⁹ modified to relate the free energies for reaction or activation to the resonance energy differences between reactants and products or transition state carbonium ions, is again adopted. Therefore

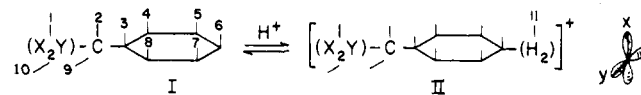
$$\Delta F \propto E_\pi(\text{ion}) - E_\pi(\text{N.M.}) - E_{H^+} = \Delta E_\pi - E_{H^+} \quad (1)$$

and

$$-RT \ln K/K_s = \Delta F - \Delta F_s = \Delta \Delta F = \mu \Delta \Delta E_\pi \quad (2)$$

E_{H^+} is the energy of the proton or protonating species, assumed independent of the reaction within a particular series; K is now either an equilibrium or rate constant, and S denotes the standard reaction, generally for the nonalkylated substrate. $E_\pi(\text{N.M.})$ is the π -electron energy of the neutral molecule and μ is the proportionality constant relating the double difference in π -electron energies to the corresponding free energies. The assumptions concerning the disposition of ΔS and ΔE_π within the ΔF and $\Delta E_{\text{electronic}}$ terms have been carried over directly from ref. 8.

The *p*-position protonation reactions of the monoalkylbenzenes, toluene, ethyl-, isopropyl-, and *t*-butylbenzene, assumed representative of strong electrophilic reactions on aromatic substrates, may be pictured as



where X and Y are hydrogen or methyl. The π -, quasi- π -framework extends over 8(10) sites in the parent aromatic and 9(11) sites in the one (two) dimensional model. Both species have 8(10) π -plus quasi- π -electrons. The π_y dimension, orthogonal to

(1) Work performed under the auspices of the U. S. Atomic Energy Commission.

(2) (a) M. J. S. Dewar, "Hyperconjugation," Ronald Press Co., New York, N. Y., 1962, and (b) J. W. Baker, "Hyperconjugation," Oxford University Press, New York, N. Y., 1952, discuss this question in great detail from widely divergent points of view.

(3) Cf. C. C. Price and D. C. Lincoln, *J. Am. Chem. Soc.*, **73**, 5836 (1951); W. A. Sweeny and W. M. Shubert, *ibid.*, **76**, 4625 (1954); V. J. Shiner, *ibid.*, **76**, 1603 (1954); A. Buraway and E. Spinner, *J. Chem. Soc.*, 3752 (1954); L. S. Bartell, *J. Chem. Phys.*, **32**, 827 (1960).

(4) R. W. Taft, Jr., and I. C. Lewis, *Tetrahedron*, **5**, 210 (1959).

(5) J. W. Baker and W. S. Nathan, *J. Chem. Soc.*, 1844 (1935).

(6) W. Markownikoff, *Ann.*, **153**, 256 (1870).

(7) Cf. P. Karrer, "Organic Chemistry," Elsevier Co., New York, N. Y., 1950, p. 54.

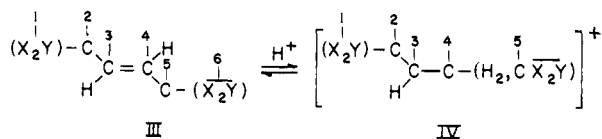
(8) S. Ehrenson, *J. Am. Chem. Soc.*, **83**, 4493 (1961).

(9) G. W. Wheland, *ibid.*, **64**, 900 (1942).

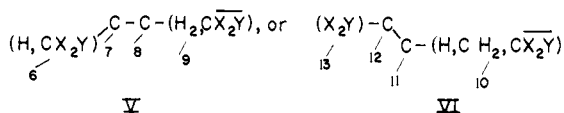
π_x , it should be noted, contains only the two orbitals of the alkyl group and two electrons.

Albeit as unstable intermediates, the existence of such ions as above is readily demonstrable (*e.g.*, from ultraviolet and n.m.r. spectra¹⁰; Olah and Kuhn have isolated a variety of salts which are stable at low temperatures¹¹). Protonation reactions of the alkyl substituted olefins are, however, less amenable to precise definition as regards the structures of their transition states. At present, informed opinion is directed to the view that in acid-catalyzed solvolyses and halogen acid additions, in particular, which shall serve as prototype reactions herein, the transition states are σ -protonated carbonium ions.¹²

A representative electrophilic addition to an olefin is, then, the formation of an isopropyl-type carbonium ion from a vicinal dialkyl substituted ethylene



These structures show the principal one-dimensional HCJ model for the reaction. Six and four delocalizable π -electrons are contained, respectively, in the olefin and ion. The orthogonal π_y dimension, which contains only quasi- π sites, is somewhat more difficultly pictured. Fixing attention on the ion, it is apparent that not only will the methyl hydrogen quasi-groups and the carbons to which they are attached constitute π_y sites, but that the central, formally sp^2 hybridized carbon is capable of participation as well. This would follow conceptually upon incorporation of the central hydrogen and one $C(X_2Y)$ group into a quasi-group, *viz.*



Two such representations, essentially identical, are seen to be possible for these ions, contrasted to one for the ethyl- and three for the *t*-butyl-type ions. The other possible π_y structures, *e.g.*, $H-C-[CX_2Y, C(H_2, \bar{X}_2Y)]$, for the isopropyl ion are assumed unimportant and ignored in the present calculations.¹³

The multiple π_y structures in the isopropyl- and *t*-butyl-type ions are incorporated into the computations by (a) assuming mutual orthogonality to each other, in addition to the formally imposed orthogonality to the π_x structure; (b) filling each Wheland-Mulliken MO; (c) cycling to self-consistency in charge densities and bond orders; and finally (d) distributing the four available quasi- π_y electrons equally among the self-consistent π_y -MO's. Interactions between these structures is accomplished by a direct coupling technique for Coulomb and overlap integrals, discussed in detail in the next section. The over-all result of this procedure is to recognize computationally the stabilization effects afforded by the second HCJ dimension, essentially

(10) C. Reid, *J. Am. Chem. Soc.*, **76**, 3264 (1954); C. Maclean, J. H. van der Waals, and E. L. Mackor, *Mol. Phys.*, **1**, 247 (1958).

(11) Cf. G. A. Olah and S. J. Kuhn, *J. Am. Chem. Soc.*, **80**, 6535 (1958).

(12) J. Manassen and F. S. Klein, *J. Chem. Soc.*, 4203 (1960); Y. Pocker, *ibid.*, 1292 (1960); J. S. Coe and V. Gold, *ibid.*, 4771 (1960); M. J. S. Dewar and R. C. Fahey, *Chem. Eng. News*, **41** (10), 38 (1963); *J. Am. Chem. Soc.*, **85**, 2245, 2248 (1963).

(13) These structures are easily seen to resemble the substituent alkyl groups themselves with only small Coulomb integral differences at site 3. Consequently, the contributions of such structures to the resonance energies should be negligible within the approximation employed.

exercised by a mechanism of charge leakage from the π_y to the formally charge deficient π_x dimension.¹⁴

3. Computations

The computational approach is the same as that described in section 3 of ref. 8 with the following major modifications:

i.—Inclusion of the second π -dimension may be viewed as expanding the secular determinant to give two orthogonal minors. Direct interactions between dimensions is therefore impossible; however, in the cycling procedure such interactions are permitted through the α , S (and β) parameters. The process of coupling of such elements recognizes the response to differential electron deficiencies or excesses between the x and y dimensions of a given site or sites, and, in fact, may be viewed in terms of self-polarizability of the atom or quasi-atom in the π -framework. Specifically

$$\alpha_i \text{ (coupled)} = \tau_{ij}\alpha_j + (1 - \tau_{ij})\alpha_i \quad (3)$$

$$\alpha_j \text{ (coupled)} = (1 - \tau_{ij})\alpha_i + \tau_{ij}\alpha_j$$

and

$$(\beta_{ij}/\beta^\circ)S^\circ \equiv S_{ij} \text{ (coupled)} = \tau_{ijkl}S_{ij} + (1 - \tau_{ijkl})S_{kl} \quad (4)$$

$$(\beta_{kl}/\beta^\circ)S^\circ \equiv S_{kl} \text{ (coupled)} = (1 - \tau_{ijkl})S_{ij} + \tau_{ijkl}S_{kl}$$

The coupling is carried out after the self-consistency adjustments and prior to re-resolution of the secular determinant. The coupling factors, τ , generally taken as 0.5, were restricted to parameters associated with the same site. Application of this technique may be illustrated by returning to the isopropyl-type ion (structures IV-VI). Sites 1 and 13; 2 and 12; 3, 7, and 11; 4 and 8; 5 and 9 are α -coupled. Bonds 1,2 and 12,13; 3,4 and 7,8; 4,5 and 8,9 are S (and β) coupled.

ii.—The inability to estimate *a priori*, parameters for the methyl-bearing quasi- π -groups with even the most modest expectations of theoretical justification has been the principal reason why C-C bond HCJ has been ignored in quantitative discussions.¹⁵ This problem is especially acute for Coulomb integral terms and seems likely to remain so for some time. Rather than guess at parameter sets, the following procedures were adopted.

(a) A grid of Coulomb integrals centered roughly about the value $\alpha = \alpha^\circ - 0.3\beta^\circ$ was considered, the central value representing the most reliable estimate for the (H_3) and (H_2) quasi-groups.¹⁶ Further, one may show that a smooth variation of α is to be expected in passing from methyl, through ethyl and isopropyl, to *t*-butyl, if free rotation of these groups is allowed. The difference in the values for these parameters, per C-C for C-H bond substitution, is, to a good approximation, equal to $\nu + 1/2\Delta E_q$, where $\nu = \omega_{H^H} - \omega_{H^{CH_3}} \cong \omega_{CH_3^H} - \omega_{CH_3^{CH_3}}$ and ΔE_q is the energy difference between the antibonding orbitals in the (H_2 , CH_3) quasi-group. (The ω -values follow Mulliken's notation.¹⁷) The question of magnitude, or, indeed, even the sign of the quantity, $\nu + 1/2\Delta E_q$, cannot be answered by presently available methods, mainly because of ν ; that a regular change in the quasi-group α 's is to be expected over the alkyl series is, however, usefully recognized.

(b) Employing the quasi-group wave functions and again assuming free rotation, the order $S_{CH_3} >$

(14) This procedure should be compared to that of N. Muller and R. S. Mulliken, *J. Am. Chem. Soc.*, **80**, 3489 (1958), where charge leakage was estimated for the ethyl ion in similar one- and two-dimensional computations. The same amount of leakage was then assumed in correcting the one-dimensional calculations for the isopropyl and *t*-butyl ions.

(15) Part of the reluctance among organic chemists to adopt this aspect of the over-all HCJ picture in even the most qualitative terms may be traced to the seeming overemphasis on the C-H bond effect for which many computations have been made. A related explanation may be found in E. Berliner, *Tetrahedron*, **5**, 202 (1959).

(16) Y. I'Haya, *J. Chem. Phys.*, **23**, 1165 (1955).

(17) R. S. Mulliken, *J. chim. phys.*, **46**, 497, 675 (1949).

TABLE I
RESULTS OF TWO-DIMENSIONAL WHELAND-MULLIKEN AND SELF-CONSISTENT CALCULATIONS ON A *p*-ALKYLBENZONIUM ION^a
 $\alpha_{H_2} = -0.3\beta^\circ$, $\alpha_{X_2Y} = -0.3\beta^\circ$

		Self-consistent						
		First iteration		S_{23} free		$S_{23} = 0.16$		
Charges on, bond orders between, π -sites ^c	1(1,2)	0.9329	0.9780	0.9284	0.9537	0.9497	0.9736	
	2(2,3)	1.0418	.1960	1.0092	.2816	1.0144	.2124	
	3(3,4)	0.7525	.5934	0.7746	.5672	0.7746	.5805	
	4(4,5)	1.0036	.7504	.9361	.7716	.9334	.7642	
	5(5,6)	0.7467	.3480	.8019	.3138	.7956	.3170	
	6(6,11)	1.0264	.8614	.9903	.8877	.9889	.8853	
	9(9,10)	1.0443	.9994	1.0161	.9999	1.0187	.9999	
	10	0.9557		0.9839		0.9813		
	11	0.7458		0.8216		0.8162		
	Energies of the doubly occupied delocalized π -MO's (units of β°)		1.58336		1.69552		1.69426	
			1.43464		1.56133		1.50856	
		1.37196 ^d		1.43319 ^d		1.41778 ^d		
		1.08234		1.19758		1.23126		
		0.80128		0.99092		0.99517		
Total delocalization energy		12.54717		13.75706		13.69405		
Total D.E. for parent aromatic		11.38658		11.50086		11.48862		
$\Delta E_{deloc.}$		1.16059		2.25620		2.20543		
$\Delta E_{deloc.}$ (benzene - benzenium ion)		1.14861			2.13878			
$\Delta \Delta E_{deloc.}$		0.01198		0.11742		0.06665		
Total delocalization energies (no α, S coupling)	Ion			13.68134		13.65081		
	Parent aromatic			11.49383		11.48494		
	$\Delta \Delta E_{deloc.}$			0.04873 ^e		0.02709		

^a Atoms numbered as in Fig. 1. ^b Carbons bearing quasi-groups always assigned $\alpha = -0.075\beta^\circ$; $\tau_{2,9} = \tau_{1,10} = \tau_{1,2,9,10} = 0.5$. Here and henceforth, $\alpha = \alpha^\circ + k\beta^\circ$ will be given as $\alpha = k\beta^\circ$ with the understanding that α° , the Coulomb integral for sp^2 -C, is arbitrarily scaled to zero. ^c All tables give Chirgwin-Coulson bond orders and charge densities; cf. ref. 8. ^d π -MO, over sites 9 and 10. ^e Difference between this and comparable value of ref. 8 ($0.04651\beta^\circ$) due to slightly different method of quasi- π -bond order adjustment.

$S_{C(H_2CH_3)}, S_{C(H(CH_3)_2)} > S_{C(CH_3)_3}$ is found. For the normal bond distances, S_{CH_3} and $S_{C(CH_3)_3}$ are computed to be 0.629 and 0.586, or in the ratio 1.00:0.93. Since differences of this magnitude should contribute only as second-order effects, all S_{quasi} values for the alkyls were taken to have the methyl value, 0.629, considerably simplifying the computations.¹⁸

iii.—Self-consistent computations on the energies of the lower lying electronic states for the alkylbenzenes were made possible by amending the ground state program with an automatic aufbau subroutine. The desired energy level occupation scheme is provided to the computer in terms of how many electrons (0, 1, or 2) are to be placed in each level taken in the order most highly bonding to most highly antibonding. This filling procedure is carried out after each iterated secular equation solution and prior to the parameter adjustment sequences. In the event of degeneracies ($<10^{-5}\beta^\circ$), the electrons designated for the degenerate levels are equally divided among the levels. (This procedure is to be conceptually distinguished from the general practice of transferring an electron from one level to another, usually bonding to *virtual* anti-bonding, both of which correspond to eigenlevels of the ground state.)

4. Particular Model Results and Interpretation

Tables I-III present some typical results obtained from the calculations. In Table I, the self-consistent charge densities and bond orders for an alkylbenzenium ion may be contrasted with the Wheland-Mulliken

(18) The MO eigenfunctions and values for the X_2Y quasi-group, tetrahedrally disposed with respect to the central carbon, are, assuming β proportional to S , $\epsilon_{AB} = \alpha_X + [\Delta - \beta_{XX}/(1 - S_{XX})]$, and $\epsilon_{AB} = \alpha_X + [P\Delta + \beta_{XX} - 4\beta_{XY}S_{XY} + (\beta^2 + 8\beta_{XY}^2 + P\Delta[2\beta_{XX} + \Delta(1 + S_{XX})])^{1/2}]/2P$ where $\Delta = \alpha_X - \alpha_Y$ and $P = 1 + S_{XX} - 2S_{XY}^2$. B and AB specify the bonding and antibonding functions, respectively. The corresponding wave functions are $\psi_{AB} = (\varphi_{X1} - \varphi_{X2})/[2(1 - S_{XY})]^{1/2}$ and $\psi_{AB} = [n\varphi_Y + (\varphi_{X1} + \varphi_{X2})]/(n^2 + 2 - 4nS_{XY} + 2S_{XX})^{1/2}$, leading to $S(CX_2Y)_B = 2 \cos \theta [nS_{CY} + S_{CX}] \sin \theta / (n^2 + 2 - 4nS_{XY} + 2S_{XX})^{1/2}$ and $S(CX_2Y)_A = \sqrt{2} \sin \theta S_{CX} / (1 - S_{XY})^{1/2}$. The CX and CY angles are θ ; n , the normalization constant, depends complexly upon the β and S parameters chosen.

TABLE II

CALCULATED SELF-CONSISTENT PROPERTIES OF THE GROUND AND FIRST EXCITED STATES OF AN ALKYL-SUBSTITUTED BENZENE,

$$\alpha_{X_2Y} = -0.3\beta^\circ$$

Charges on, bond orders between, π -sites	Ground state		Excited state ^e	
	1(1,2)	0.9753	0.9852	0.9870
2(2,3)	1.0209	.1693	.9964	.2482
3(3,4)	0.9997	.6568	1.0098	.3254
4(4,5)	1.0012	.6687	1.0068	.8316
5(5,6)	1.0003	.6655	0.9965	.3529
6	1.0010		1.0000	
9(9,10)	1.0218	0.9999	1.0020	1.0000
10	0.9782		0.9980	
Energies of the delocalized π -MO's occupation number		1.47283(2)		1.47706(2)
		1.39845(2) ^d		1.40817(2) ^d
		1.29496(2)		1.29499(2)
		0.80163(2)		0.80030(2)
		0.77644(2)		0.77393(1)
	-1.29447(0)		-1.30350(1)	
Total delocalization energy		11.48862		9.43147
$\Delta E, \Delta E_{benzene}, \Delta \Delta E$ Self-consistent		2.05715	2.13431	0.07716
	First iteration	2.07014	2.13107	.06093
	S.C. virtual orbitals	2.07091	2.13431	.06340

^a Footnotes a to d of Table I apply; S_{23} held at 0.16. ^e Restriction of geometry to that of ground state makes these bond orders nonself-consistent with respect to bond lengths.

(first iteration) results. More charge is seen to be transferred from the alkyl group to the quasi- π -group formed by protonation, and considerable smoothing of the ring charges also occurs upon making the calculation self-consistent. Also, the relative stabilization energy for reaction, *i.e.*, that attributable to the presence of the alkyl group, is dramatically enhanced by this procedure. Coupling the α and S elements does very little in the neutral aromatic, a not surprising result in light of the minor effects of alkyl substitution on the resonance energies of these molecules. For the ions the

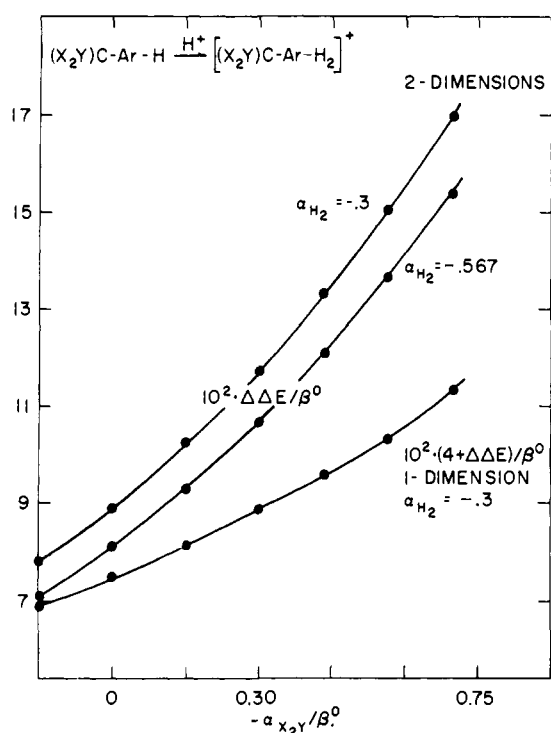


Fig. 1.—One- and two-dimensional model $\Delta\Delta E$ vs. quasi- π -group Coulomb integral values for the alkylbenzene protonation reactions.

coupling effect is considerably larger, reflecting the importance of charge leakage from one dimension of the alkyl group to the other and thence to the ring.

Another refinement of the model was considered. Some results bearing on this are to be found in the last column of Table I. Two sources of uncertainty are involved in adjustment of the overlap integral for the bond between the ring and substituent alkyl group. The first is whether the linear adjustment of S with bond order (p) employed for the ring bonds is applicable (*i.e.*, $S = 0.195p + 0.080$),⁸ or for that matter whether a linear relationship is valid at all. The second arises from the well known tendency of Hückel and related MO theories to overemphasize bonding, as measured by bond order, between atoms which are "single-bonded" in their principal resonance structure (*cf.* p_{23} in butadiene).¹⁹ Presently lacking means to resolve these uncertainties, the extreme cases where S_{23} , structures I and II, are held at 0.16 have been examined. The latter value is based upon the known bond length in the neutral aromatics and should represent a minimum in bonding and therefore also in stabilization in the ions (*i.e.*, the nonself-consistent S_{23} should preclude the full measure of direct HCJ). The results of Table I indicate this to be so. Of greater general importance is the observation that the $\Delta\Delta E$ values over the entire range of quasi-group coulomb integrals run parallel for S_{23} allowed free variation, compared to S_{23} held constant at 0.16 (Fig. 1). The ratio, in this order, is 1.7575 ± 0.0035 . The value of μ , eq. 2, as yet unspecified, may now incorporate this ratio allowing effective interchangeability between models. The implication of including these refinements (the second dimension and variation of S with p) on former conclusions reached for the methylbenzene basicity series⁵ should not be overlooked. Values of μ ranging between 0.9 to 1.6, necessary to bring the three sets of experimental data into line with each other, and with theory, may now be

(19) An interesting discussion of this and closely related subjects is to be found in N. Ham, *Rev. Pure Appl. Chem.*, **11**, 159 (1961).

TABLE III
RESULTS OF ONE- AND TWO-DIMENSIONAL SELF-CONSISTENT CALCULATIONS ON A REPRESENTATIVE ISOPROPYL-TYPE CARBONIUM ION FORMATION REACTION^a

Structure IV: $\alpha_1 = -0.3\beta^0$, $\alpha_3 = -0.567\beta^0$, $\alpha_6 = \alpha_{10} = -0.3\beta^0$	One dimension		Two dimensions		
Charge deficiencies	1(1,2)	0.1847	0.8857	0.1586	0.9005
on, ^b bond orders	2(2,3)	.0235	.4477	.0097	.4967
between, π -sites	3(3,4)	.5086	.5176	.4938	.5545
	4(4,5)	.0170	.8448	.0097	.8890
	5	.2663		.2314	
	60576	
	100585	
Energies of the delocalized π -MO's, occupation number		1.71782(2)		1.90418(1) ^c	
		1.46717(2)		1.89029(1) ^d	
		0.42911(0)		1.68767(2)	
				1.48083(2)	
				1.44219(1) ^c	
				1.35492(1) ^d	
				0.36746(0)	
Total delocalization energy		6.36998(4)		12.92858(8)	
Total localization energy		5.32537		10.93190	
Resonance energy		1.04461		1.99668	
Resonance energy of parent olefin, <i>e.g.</i> , 1-butene ^e		0.01327		0.03656	
ΔE		1.03134		1.96012	
ΔE (ethylene - ethyl ion) ^e		0.79243		1.88724	
$\Delta\Delta E$.023891		0.07288	

^a Atoms numbered as in structures IV-VI. Total charges and bond orders computed for two-dimensional case by summing over these structures. ^b Units of $-e$. ^c π_{y1} . ^d π_{y2} . ^e Implies $\alpha_{(H_2, CX_2Y)} = -0.3\beta^0$, $\alpha_{H_3} = \alpha_{H_2} = -0.567\beta^0$; this is a sample, not necessarily a final, choice of parameters; see text.

derived solely from the HCJ models in various degrees of refinement. Theoretical evaluation of the effects of induction are thereby rendered more uncertain than was previously suggested.²⁰

Turning from reactivities for the moment, Taft and Lewis⁴ were able to extend their correlations to the differential effects of alkyl groups on the ultraviolet spectra of substituted benzenes. Specifically, the data of Matsen, *et al.*,²¹ on the frequencies of the O-O transitions were found to exhibit a clear-cut Baker-Nathan order. Theoretical investigation was carried out employing the modified ground state program previously described; a typical result is found in Table II.²² In

(20) S. Ehrenson, *J. Am. Chem. Soc.*, **84**, 2681 (1962). A recent paper by R. L. Flurry, Jr., and P. G. Lykos, *ibid.*, **85**, 1033 (1963), provides an interesting comparison. They employed a modified Pariser-Parr-Pople model for induction and found a least squares value of 0.69 for μ would correlate the methylbenzene basicity data of Mackor, *et al.* [*Trans. Faraday Soc.*, **54**, 186 (1958)], quite satisfactorily.

(21) F. A. Matsen, W. W. Robertson, and R. L. Chuoke, *Chem. Rev.*, **41**, 273 (1947). The Baker-Nathan order is found both in the vapor and solution phases. These results should be contrasted with those obtained for alkyl-substituted nitrobenzenes; *cf.* Shubert, *et al.*, *J. Am. Chem. Soc.*, **79**, 930 (1957), where the spectral shifts in the vapor phase follow the inductive order. As Taft and Lewis have pointed out in ref. 4, however, in the latter studies the spectral bands were not resolved in terms of the O-O frequencies. Substantial inductive effects may be operative in the nitrobenzene transitions reported.

(22) Amplification of several of the details of these calculations is necessary. Since the transitions are vertical Franck-Condon transitions, the geometry of the excited and ground states must be the same. This is accomplished by by-passing the bond-order-overlap adjustment after starting with the S.C. ground state geometry. No distinction between singlet and triplet states is made, nor is the level splitting due to degeneracy in benzene considered. The familiar weighted mean state approximation²³ is employed under which the transitions of interest for benzene are: $(X_0)^2 \rightarrow (X_1)^2(X_{=1})^3(X_{=2})$ and correspondingly for the alkylbenzenes $(X_0)^2(X_{A1})^2(X_1)^2(X_2)^2(X_3)^2 \rightarrow (X_0)^2(X_{A1})^2(X_2)^2(X_3)^2(X_4)$.

(23) *Cf.* C. C. J. Roothaan and R. S. Mulliken, *J. Chem. Phys.*, **16**, 118 (1948).

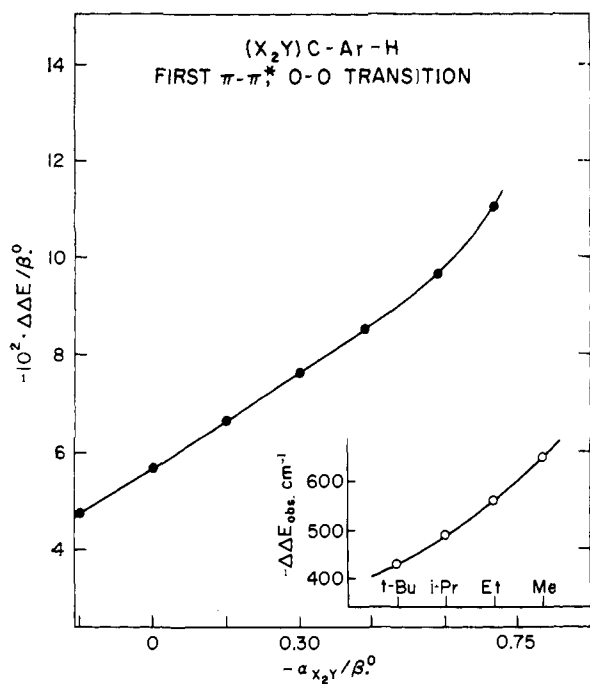


Fig. 2.—Computed transition energies for the alkyl-substituted benzenes, referenced to benzene, as a function of quasi- π -group Coulomb integral.

accordance with intuition, π -electronic charge is seen to be released from the alkyl group to the ring (>0.01 electron), thereby stabilizing the excited state and lowering the O-O transition energy relative to that of benzene. Of further interest, and beyond qualitative expectations, the release is predicted to occur most strongly to the ring atom bearing the alkyl group and somewhat more weakly to the *o*-positions. The small transition dipole predicted is in agreement with the relatively small extinction coefficients noted for these transitions; from ref. 21, $\epsilon_{\max} < 200$. Comparing the $\Delta\Delta E$ results, the two-state model energy is 20% greater than that of the first iteration or virtual orbital models. Considering the charge differences between states, this rather unimportant difference might have been expected; the ω -technique results were computed, however, to preserve the consistency of approach toward all phenomena examined.

Table III presents several details on the third of these phenomena, *i.e.*, on an alkyl carbonium ion presumed to represent the transition state structure of an olefin undergoing protonation. The energy and charge redistribution effects accompanying the inclusion of the second π -dimension are the most striking feature of these results. As was noted for the aromatic ion, π_y -charge leakage is accompanied by increased stabilization of the ion, relative to its parent. Unlike the aromatic case, however, the $\Delta\Delta E$ value is decreased under this refinement. This may be attributed directly to stabilization of the ethyl ion. The latter gains most from electron leakage; in the one-dimensional model the formal positive charge could be spread over only two π -sites. (Contrast to the reference benzenium ion!) As for the charges, details of the interdimension leakage are essentially summarized by the deficiencies noted in the π_y -quasi-atom sites 6 and 10. Some of this charge goes directly to relieve the deficiency on the central atom 3; a good bit more goes indirectly to the same purpose by increasing the bond orders 2-3 and 3-4.²⁴

(24) Examination of the charges on the terminal quasi-atoms suggests at first glance that most of the leakage occurs to these positions. It should be

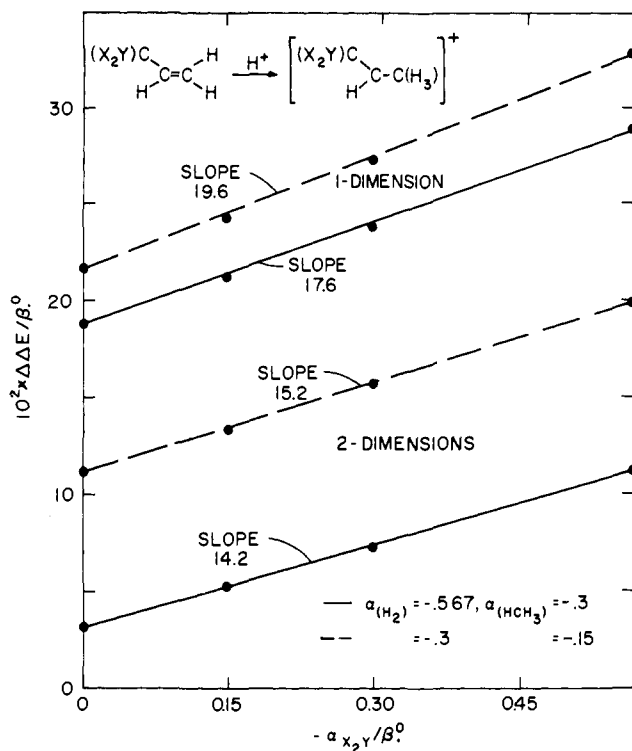


Fig. 3.—One- and two-dimensional model $\Delta\Delta E$ vs. quasi- π -group Coulomb integral values for the propylene-type molecule protonation reactions.

5. Theory, Addition Rules, and the Baker-Nathan Effect

General results bearing directly on the Baker-Nathan effect are now considered. In Fig. 1, the variation of $\Delta\Delta E$ for alkylbenzenium ion formation with Coulomb integral of the alkyl quasi-group is shown. It is apparent from these results that the greater the electropositivity of this group, the more favorable is the protonation reaction predicted to be. Therefore, if the Baker-Nathan order is to be followed, we must conclude $\alpha_{Me} < \alpha_{Et} < \alpha_{i-Pr} < \alpha_{t-Bu}$. Upon examination of Fig. 2, the same conclusion is demanded if the decreased experimental red shift in passing from toluene to *t*-butylbenzene is recognized. The variations in extinction coefficient observed by Matsen²¹ for the series are likewise in agreement with this conclusion. These are especially useful results in that the electronic rearrangements involved in these transitions are felt to be essentially conjugative²⁵ and uncomplicated by the possibility of appreciable inductive effects, which may complicate reactivities. Figure 3, representing the energetics of Markownikoff olefin protonation, likewise requires this ordering of Coulomb integrals if we are to accept a Baker-Nathan order for these reactions. The results are clearly consistent. The question arises whether they agree with chemical intuition otherwise obtained as to the effects, individual and total, of the alkyl groups as substituents.

Perhaps the most immediate query concerns rationalization of the inductive order, which is the reverse of the HCJ order and seemingly in disagreement with the Coulomb order presented above. If only quasi- π -effects of the alkyl groups are to be considered, the opposed HCJ and inductive effects would be difficult to rationalize on the basis of the present models. That a

recognized, however, that these sites are themselves involved in construction of sites 6 and 10, suggesting such a conclusion to be unwarranted.

(25) Cf. J. R. Platt, *J. Chem. Phys.*, **19**, 101 (1951); L. Goodman and H. Shull, *ibid.*, **27**, 1388 (1957).

quasi- σ -bond necessarily accompanies the formulation of quasi- π -bonds from the formally tetrahedral CX_2Y group must, however, not be overlooked. And it is to this σ -bond that the bulk of inductive effects must be attributed. If, now, the possibility of differing orders of electropositivities for the quasi- σ - and π -bonds over the alkyl group series is allowed, the inductive and HCJ orders are easily rationalized. That such a difference may exist is a corollary to Mulliken's intramolecular two-way charge transfer theory,²⁶ and is in harmony with the variable orbital exponent results of refined SCF theory for electrons in orbitals with the same principal quantum number.²⁷

Some semiquantitative arguments may be advanced to show that these bond properties may very well vary in the proposed manner. Muller and Mulliken²⁸ have shown that a rough measure of the electronegativity of quasi- π - and σ -groups may be had from their respective ionization potentials, the latter being computed from the appropriate bonding and antibonding character of the quasi-MO's (see also section 3 iia). For simplification the (H_2) and $(CH_3)_2$ groups are examined.

$$(\alpha_\pi)_H \propto I_{H=H} = I_H \pm \beta_{HH} (1 \mp S_{HH}) \quad (5)$$

and

$$(\alpha_\pi)_{(CH_3)_2} \propto I_{CH_3=CH_3} = I_{CH_3} \pm \beta_{CH_3CH_3} (1 \mp S_{CH_3CH_3}) \quad (6)$$

Now, if $I_{sp^3CH_3} \leq I_H$, as seems likely,²⁹ and $\beta_{HH} \approx -2$ e.v., $S_{HH} \approx 0.25$,¹⁷ then $|\beta_{CH_3CH_3}/(1 + S_{CH_3CH_3})|$ would have to be greater than 1.6 e.v. to make the CH_3-CH_3 quasi- σ -group more electronegative than the corresponding H-H σ -group. Considering the CH_3-CH_3 distance in the *t*-butyl group, for example, (>2.6 Å.) and the necessary twist to align bonds ($\sim 71^\circ$), this value would seem unreasonable.

Opposing inductive and HCJ orders appearing consistent with the MO model, at least as far as it now seems possible to argue, the question of scaling the alkyl group parameters arises. If α_{H_3} is $-0.3\beta^\circ$ relative to sp^2 -carbon, $\alpha_{(CH_3)_3}$ must be less than $-0.3\beta^\circ$, with the other alkyl parameters, following previous arguments, intermediate between these values. Some more precise estimates are available upon examination of the Taft equation results. For a large number of reactivities correlated with the latter, a C-H to C-C bond resonance effect ratio, h_H/h_C , essentially constant at a value of 1.3, is found. Since, in Taft's notation, $R = n_H h_H + n_C h_C = \log k^p/k^0 - I$, the various R ratios and, therefore, h_H/h_C are directly equatable to the $\Delta\Delta E$'s. For methyl and *t*-butyl

$$3h_H/3h_C = h_H/h_C = \Delta\Delta E(\text{Me})/\Delta\Delta E(\textit{t-Bu}) = 1.3$$

With α_{H_3} equal to $-0.3\beta^\circ$, $\alpha_{(CH_3)_3}$ values of $-0.08\beta^\circ$, $-0.02\beta^\circ$, and $-0.04\beta^\circ$ are derived from the one- and two-dimensional alkylbenzenium ion and ultraviolet transition results, respectively. These are satisfactorily consistent results, in harmony with foregoing arguments relating α to the ionization potentials of constituent atoms or groups. (*Viz.*, $I_{CH_3-CH_3}$ should be from this result approximately equal to $I_{2p\pi C}$ or ~ 11 e.v. If $\beta/(1 - S) \cong 1-1.5$ e.v., then $I_{sp^3CH_3} \cong 12-12.5$ e.v., or ~ 2 e.v. higher than the ionization potential for

(26) R. S. Mulliken, *Tetrahedron*, **5**, 253 (1959).

(27) M. J. S. Dewar, ref. 2a, pp. 35-40, argues a closely related point, *i.e.*, how can α_{H_3} , being less than zero in the HCJ model, account for methyl's donor ability by induction. Overlooking the quasi- σ -bond, he concludes the HCJ model is responsible for the apparent anomaly.

(28) N. Muller and R. S. Mulliken, *J. Am. Chem. Soc.*, **76**, 4770 (1954).

(29) $I_{sp^3CH_3} < 10$ e.v. Distortion of the isoelectronic radical ion NH_3^+ from its planar ground state to a pyramidal structure (110°) should require less than 0.4 e.v. according to J. Higuchi, *J. Chem. Phys.*, **23**, 2197 (1955); **24**, 535 (1956). Assuming the same energy difference for CH_3^+ , planar to tetrahedral, more than 4 e.v. difference would have to exist for CH_3^+ to have $I_H < I_{sp^3CH_3}$.

the planar methyl radical; $\beta_{HH}/(1 - S_{HH}) \cong 2.7$ e.v.)

Comparison with the aliphatic ion results, Fig. 3, is now pertinent. With $\alpha_{(CH_3)_3}$ equal to $-0.05\beta^\circ$, an average of the previously obtained values, $\Delta\Delta E(\text{Me})/\Delta\Delta E(\textit{t-Bu})$ equals 1.24 and 1.30 for the one- and two-dimensional calculations. Again internal consistency is found; interestingly, here the empirical results would not have led one to expect it. Taft and Kreevoy³⁰ found larger ratios for the few olefin addition reactions which have been studied. For acetal and ketal hydrolyses and substituted ethylene and carbonyl function hydrogenations, h_H/h_C values on the order of 2 were found. However, it should be noted that these cases do not conform as well to the prototype reaction as the aromatics do to theirs, and that a much smaller amount of data is available. Further, concern over the use of enthalpies in the H_2 addition correlations, and over the method of separation of inductive effects in these systems,³¹ make these high ratios suspect.

From the results obtained here, which are essentially independent of the degree of refinement of the model and *totally independent of choice of values for μ and β°* , the suggestion is made that h_H/h_C is constant for all reactions where HCJ may be expected to play an important role. The value of 1.3 is empirically and semi-theoretically acceptable; the π -Coulomb integrals for Me, Et, *i*-Pr, and *t*-Bu are therefore taken to be -0.30 , -0.22 , -0.14 , and $-0.05\beta^\circ$, respectively.

An interesting absolute energy comparison is easily obtained from Fig. 2. The bathochromic shift of toluene relative to *t*-butylbenzene is ~ 210 cm.⁻¹ or 0.026 e.v. and is well correlated by the R terms alone in the Taft equation.⁴ The corresponding theoretical difference is $-0.016\beta^\circ$, or 0.042 e.v., in good agreement with experiment. A μ -value of 0.62 applies; values less than unity are generally required for fitting π -electron theory results to spectra, a trend which is not changed by imposition of the ω -technique or the two-state model.

Table IV presents complete results from the olefin-protonation calculations and raises several further points of interest. Most striking are the energetics predicted for the anti-Markownikoff additions. Assuming protonation of the propylene-type olefins in the substituted position results in conventional *n*-propyl-type carbonium ions, a correct Markownikoff order is obtained (*i.e.*, protonation takes place preferentially at the position of minimum alkyl substitution). Similarly, the Saytzeff-Wagner rule is also confirmed, in that in the 2-butene-type reactions, the proton preferentially adds to the carbon bearing the least electropositive alkyl, *i.e.*, *t*-butyl.

That the rates of formation for the *n*-propyl-type ions are predicted to be slower than for the reference ethyl ion is, however, a less satisfactory result in terms of general chemical intuition. Invoking HCJ as the only driving force for these reactions, and assuming only conventional carbonium ion transition states, one may easily show that such a result is demanded. The group (H_2, CX_2Y) is less π -electropositive than (H_3) and must therefore stabilize the *n*-propyl ions, which are for the purposes of the HCJ model merely α -

(30) R. W. Taft, Jr., and M. M. Kreevoy, *J. Am. Chem. Soc.*, **79**, 4011 (1957); **77**, 5590 (1955).

(31) R. W. Taft, Jr., private communication. Part of the problem may lie in the relation of X as substituent when bonded directly to the olefinic system compared to when a methylene group is interposed. A related point regarding definition of substituent and standard in previous theoretical work⁸ deserves mention. There, quasi-groups formed by protonation of the methylbenzenes were erroneously considered as legitimate *l.f.e.* substituents. The correct h_H/h_C ratio was fortuitously obtained from these groups even though the electropositivity of (H_3, CH_2) was then assumed to be greater than that of (H_3) !

TABLE IV
SELF-CONSISTENT π -ELECTRON ENERGIES FOR PROPYLENE,
2-BUTENE, AND ISOBUTYLENE-TYPE OLEFIN PROTONATION
REACTIONS^a

Propylene-type ^b (X ₂ Y)CHC=CH ₂						
α_{X_2Y}	$10^2 \times \Delta\Delta E$					
	Isopropyl ion ^c		<i>n</i> -Propyl ion ^c		Cyclic ^d	
	1 Dim.	2 Dim.	1 Dim.	2 Dim.		
0	21.61	11.15	-3.75	-4.96	...	
-0.15	24.38	13.35	-3.77	-5.06	22.83 ^e	
- .30	27.27	15.64	-3.92	-5.22	24.06	
- .567	32.81	19.93	-4.68	-5.45	25.80	

2-Butene-type, ^c (X ₂ Y)CHC=CHC(X ₂ Y)						
1	2	Protonation position				
		1		2		
α_{X_2Y}	α_{X_2Y}	1 Dim.	2 Dim.	1 Dim.	2 Dim.	
0	0	18.13	7.34	
	-0.567	30.18	16.47	
-0.15	0	18.16	7.11	21.50	10.08	
	-0.567	30.20	16.23	20.66	9.59	
- .30	0	18.00	6.95	24.50	12.11	
	-0.567	30.05	16.09	23.66	11.62	
- .567	- .567	29.34	15.98	

Isobutylene-type, ^f C(X ₂ Y)C(X ₂ Y)C=CH ₂					
α_{X_2Y}	$10^2 \times \Delta\Delta E$				
	$\alpha_{X_2Y} = -0.3\beta^\circ$		$\alpha_{X_2Y} = -0.15\beta^\circ$		
	1 Dim.	2 Dim.	1 Dim.	2 Dim.	
0	41.36	31.95	38.86	30.10	
-0.15	43.26	32.76	41.12	31.96	
- .30	45.32	34.66	43.26	32.76	
- .567	49.29	38.87	47.40	37.08	

^a References to the ethylene reaction; $\Delta E(1 \text{ dim.}) = 0.69615(2 \text{ dim.}) = 1.73591$. $\alpha_{H_3} = \alpha_{H_2} = -0.30$. All energies and Coulomb integrals in units of β° . ^b $\alpha_{H_2CX_2Y} = -0.15$. ^c $\alpha_{(H_2CX_2Y)} = \frac{1}{2}(-0.15 + -0.3) = -0.225$. ^d Represents maximum stabilization through choice of symmetric cyclopropanium ion structure (see text). Computations are 1-dimensional. ^e Extrapolated from the other two values given. ^f All protonations are Markownikoff.

modified ethyl ions, less than the reference ethyl ion is stabilized by the (H₃) group.

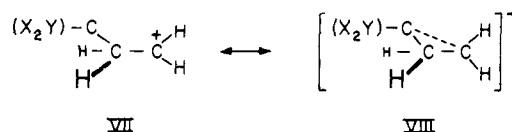
Several ways of rationalizing this apparent anomaly merit discussion. The first and probably weakest is that chemical intuition is incorrect. There seem to have been no experimental results published where anti-Markownikoff products were detected in the proven absence of other addition mechanisms, *i.e.*, radical additions.³² Little may be concluded, however, from this lack of information; even if the energetics were the same as for ethylene, the rate would still be 10^{-7} that for isopropyl ion formation (from Table IV with $\alpha = -0.3\beta^\circ$ and $\beta^\circ = -60 \text{ kcal.}$).

If chemical intuition is correct, important effects of induction, formally ignored in the present models, must be considered. The inductive order as previously noted is in the correct direction to reverse the HCJ-imposed order. It should be noted at the same time that a massive inductive effect must be postulated, if the results of Table IV are accepted as reasonable estimates of HCJ. Again, employing the dual substituent linear free energy equation, with σ^* values for methyl and ethyl relative to hydrogen as standard, a $\rho^* \sim -40$ (1 dim.) or ~ -50 (2 dim.) is necessary to bring the *n*-propyl ion formation rate up to that for the ethyl ion. To have the *n*-propyl rate intermediate between the ethyl and isopropyl ion rates requires a $\rho^* \sim -200$. These magnitudes are much too great, even if HCJ is overestimated by a factor of two, as the ultraviolet spectra correlation tends to suggest. On the other hand, the ρ^* necessary to put the propylene and 1-butene results of Table IV on Taft's scale is ~ -15 ,

(32) M. S. Kharasch and co-workers, *J. Am. Chem. Soc.*, **56**, 1782 (1934), and other papers, claim exclusive Markownikoff addition of halogen acids to various olefins when radical reactions are suppressed.

(~ -8 employing the above-mentioned HCJ factor), assuming no inductive effect. Whatever the latter effect contributes would decrease the magnitude of ρ^* .³³ We may conclude, then, that while induction should play some part in the ordering of the reactivities considered, its neglect is not likely to be solely responsible for the anti-Markownikoff results obtained.

Another and most intriguing way the *n*-propyl ion can be stabilized is through a cyclic or nonclassical carbonium ion structure in the transition state. In



the symmetry limit and with X₂Y being H₃, this structure represents protonated cyclopropane, a close relative of the previously examined benzenium ion. Much attention has been paid to this and similar structures in an attempt to rationalize various carbonium ion reactions in the vapor as well as solution phases.³⁴ Considerable controversy surrounds the question of their importance; the existence of at least one such ion seems to have been demonstrated, however.³⁵

Carrying out one-dimensional calculations with the (H₂) and (H₃) groups permitted to hyperconjugate, the results in the last column of the first section of Table IV were obtained. Because of the relative crudeness of these computations (*e.g.*, the symmetrical structure was used, aromatic bond order, charge density adjustments were made, and no consideration was given to ring strain), no quantitative or even semi-quantitative conclusions are possible. Nevertheless, it seems quite plausible, from these results, that such structures may appreciably stabilize β -alkyl substituted carbonium ions, relative to those not so substituted, where three or more carbon ring structures are not possible.

Several other results on the olefin-alkyl ion systems deserve mention. The $\Delta\Delta E$ variation with α is very nearly linear, Fig. 3, as contrasted with the noticeable upward concavity for the aromatic series, Fig. 1. The reason for this is not apparent; perhaps it is due to the essential intra-ion uniformity, a factor which so complicated the formulation of models for these entities.

The formation of the *n*-propyl-type ions from propylenes and isopropyl-type ions from the 2-butenes involves localization of quasi- π -electrons when the groups (H₂, CX₂Y) are formed. The $\Delta\Delta E$ differences over the various (X₂Y) groups, Table IV, are then simply reflections of the differences in the energies of the parent olefins. And, finally, in the isobutylene reactions to form *t*-butyl-type ions, approximate additivity of HCJ effects upon multiple substitution is found. In general, a slight leveling is noted in the one-dimensional results while a slight enhancement is found using the two-dimensional model. Either result thereby agrees with the linear free energy correlation conclusions for multiple substitutions.

6. Conclusions

From the results reported herein and previously by the author,^{8,20} it appears that hyperconjugation may play an important or even dominant role in the rates

(33) Large negative ρ 's have been reported for electrophilic aromatic reactions, *e.g.*, -12 for the bromination (Br₂) of benzenes. (*Cf.* P. B. De la Mare, *J. Chem. Soc.*, 4450 (1950). Taft and Kreevoy³⁰ have found $\rho^* = -3.6$ in acetal and ketal hydrolyses.

(34) *Cf.* P. N. Rylander and S. Myerson, *J. Am. Chem. Soc.*, **78**, 5779 (1956); P. S. Skell and I. Starer, *ibid.*, **84**, 3962 (1962); P. D. Bartlett, E. R. Webster, C. E. Dills, and H. G. Richey, Jr., *Ann.*, **623**, 217 (1959).

(35) P. von R. Schleyer, D. C. Kleinfelter, and H. G. Richey, Jr., *J. Am. Chem. Soc.*, **85**, 479 (1963).

of, or positions of equilibrium for, some carbonium ion-forming reactions. HCJ models of various degrees of refinement all indicate this effect to be important, at least for the reactions where isovalent hyperconjugation may be invoked. From prototype protonation reactions considered, empirical reactivity rules (*i.e.*, Baker-Nathan, Markownikoff, and Saytzeff-Wagner) and the results of linear free energy equation correlations are found to be fairly well represented by theory. Consistency is also noted for the theoretical explanation of the ultraviolet red shifts accompanying alkylations of benzene. Operational distinctions between the one- and two-dimensional HCJ models, with or without various refinements, are not possible from the work reported here; it is gratifying in a sense that the general conclusions forthcoming are independent of the "goodness" of the model.

These results are generally consistent with the assignment of greater π -electropositivity to the methyl (H_3) than to the *t*-butyl $(CH_3)_3$ quasi- π -group. It does not seem unlikely, at the same time, that this order is different for the quasi- σ -groups, which, it is felt, operate quantum chemically in terms of induction. The possibility that such inductive effects are also important in stabilizing carbonium ions is suggested from the apparent anomalous ordering of the *n*-alkyl *vs.* ethyl ions by the HCJ models. That cyclic or nonclassical structures may also influence the energetics of such ion-producing reactions should also, it appears, be seriously considered.

Acknowledgment.—It is a pleasure to acknowledge the interest of Dr. R. Moccia who provided considerable help in construction of the IBM 709-7090 computer program used in this work.

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, GEORGIA INSTITUTE OF TECHNOLOGY, ATLANTA, GA.]

Carbanions. VII. Cleavage of 2,2-Dimethylpropyl-, 2,2,2-Triphenylethyl-, and 3,3,3-Triphenylpropyltrimethylammonium Iodides by Sodium in Liquid Ammonia¹

BY ERLING GROVENSTEIN, JR., AND LYNN CALLOWAY ROGERS

RECEIVED SEPTEMBER 3, 1963

The cleavage of 2,2-dimethylpropyltrimethylammonium, 2,2,2-triphenylethyltrimethylammonium, and 3,3,3-triphenylpropyltrimethylammonium iodides with sodium in liquid ammonia at -33° gives statistically corrected ratios of products, $3(RH)/(CH_4)$, for cleavage of the large alkyl group *vs.* methyl of 0.0125 ± 0.0020 , $10,000 \pm 2000$, and 92 ± 16 , respectively. These results are accounted for on the basis of cleavage of groups as carbanions, with electronic rather than steric factors being of dominant importance in determining the ease of cleavage of groups. While the product from cleavage of the 2,2-dimethylpropyl group was simply 2,2-dimethylpropane, that from cleavage of 2,2,2-triphenylethyl was mostly 1,1,1-triphenylethane accompanied by some 1,1,2-triphenylethane and diphenylmethane. The 1,1,2-triphenylethane is believed to be formed by rearrangement of the 2,2,2-triphenylethyl carbanion. It was shown that diphenylmethane (along with toluene) could result from cleavage of 1,1,2-triphenylethane. Reaction of 2,2,2-triphenylethyl chloride with sodium in liquid ammonia gave similar products to those obtained from 2,2,2-triphenylethyltrimethylammonium iodide except that appreciable triphenylethylene was also formed. Reaction of 2,2,2-triphenylethyltrimethylammonium iodide with molten sodium in boiling dioxane gave very different ratios of products from those produced in liquid ammonia. It was demonstrated that at the boiling point of dioxane, 2,2,2-triphenylethyltrimethylammonium iodide is decomposed partially to methyl iodide and *N,N*-dimethyl-2,2,2-triphenylethylamine. Reaction of 2,2,2-triphenylethyltrimethylammonium iodide with sodium or potassium amide gave, under appropriate conditions, an excellent yield of *N,N*-dimethyl-3,3,3-triphenylpropylamine and a little triphenylethylene. The former seems to be formed by a Stevens rearrangement and the latter by an α -elimination with rearrangement. Cleavage of the 3,3,3-triphenylpropyl group from 3,3,3-triphenylpropyltrimethylammonium iodide by sodium in liquid ammonia gave much 1,1,1-triphenylpropane accompanied by equimolar amounts of ethylene and triphenylmethane. The first product appears to result from protonation of the 3,3,3-triphenylpropyl carbanion and the latter products from a fission reaction of this carbanion.

On the basis of studies of the cleavage of tetraalkylammonium halides by sodium in dioxane^{2a} and in liquid ammonia,² it was concluded that methyl and higher primary alkyl groups (Et, *n*-Pr, *n*-Bu) probably cleave from nitrogen as carbanions while secondary and tertiary alkyl groups predominantly cleave as free radicals. While the relative rates of cleavage are primarily due to the destabilizing or stabilizing effect of α -alkyl groups, respectively, upon incipient carbanions or radicals in the transition state for cleavage, calculations indicate that in some cases steric acceleration may be of importance. The present work was undertaken in order to study further electronic and steric effects in cleavage of primary alkyl groups. Toward this end, 2,2-dimethylpropyl-, 2,2,2-triphenylethyl-, and 3,3,3-triphenylpropyltrimethylammonium iodides have been cleaved by sodium in liquid ammonia.

Reaction of 2,2-Dimethylpropyltrimethylammonium Iodide with Sodium in Ammonia.—This quaternary

ammonium salt was completely soluble in the liquid ammonia solutions used. The results from reaction with sodium in liquid ammonia are recorded in Table I. Only methane and neopentane were found in the gaseous hydrocarbons produced in these reactions. Identification of products was based on retention times in vapor phase chromatographic analysis. Under the conditions employed, methane and neopentane could be readily distinguished from 2-methylbutane, 1,1-dimethylcyclopropane, *n*-pentane, and 2-methyl-2-butene. β -Elimination, which has always previously^{2b} been a side reaction in cleavage of *n*-alkyl groups from quaternary nitrogen under similar conditions, is impossible in the present case because of absence of β -hydrogen atoms. The absence of detectable amounts of 1,1-dimethylcyclopropane and 2-methyl-2-butene demonstrates in the present cleavage that reductive fission of alkyl groups takes place more readily than α -elimination which would be expected to give rise to such products.³

The ratio of neopentane to methane from cleavage of 2,2-dimethylpropyltrimethylammonium iodide, after multiplication by a statistical factor of three to correct

(1) Presented in part at the Symposium on Carbanions, 144th National Meeting of the American Chemical Society, Los Angeles, Calif., April 2, 1963. For more complete experimental details see the M.S. thesis of L. C. Rogers, Georgia Institute of Technology, September, 1962.

(2) (a) E. Grovenstein, Jr., E. P. Blanchard, Jr., D. A. Gordon, and R. W. Stevenson, *J. Am. Chem. Soc.*, **81**, 4842 (1959); (b) E. Grovenstein, Jr., and R. W. Stevenson, *ibid.*, **81**, 4850 (1959).

(3) L. Friedman and J. G. Berger, *ibid.*, **82**, 5758 (1960); **83**, 492, 500 (1961); P. S. Skell and A. P. Krapcho, *ibid.*, **83**, 754 (1961).