

130. *The Effect of Deuteration on Electron Distribution and Energy of Conjugated Molecules. Part III.* LCAO-MO Treatment of Ethyl-carbonium Ion and its Methyl-deuterated Analogue.*

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The effect of deuteration in the methyl group on the π -electron energy and charge distribution of the static model of ethyl carbonium ion $\text{CH}_3\cdot\text{CH}_2^+$ is investigated, by the LCAO-MO treatment. The principal effects are those of increased $\text{D}_3=\text{C}$ overlap and increased effective electropositivity of the D_3 pseudoatom, which oppose one another. The combined effect cannot be determined unambiguously, but the calculations are consistent with hyperconjugative destabilisation of the deuterated carbonium ion, which may be significant in connection with solvolytic secondary isotope effects.

In Part II * of this series we discussed the effect of deuteration in the methyl group on the energy and electron distribution of toluene. The two principal factors in that system were (i) the greater effective electropositivity of the D_3 pseudoatom relative to the methyl-carbon atom and (ii) the increased overlap between the orbitals of appropriate symmetry in the $\text{D}_3=\text{C}$ group.

In the present paper we extend the investigation to positively charged molecules such as alkyl carbonium ions. Our interest in this problem arose from observation of secondary isotope effects in solvolysis,^{1,2} where it appears that deuteration on the carbon atom beta to the leaving group generally decreases the rate of solvolysis to the extent of from several percent to several tens of percent. Effects of this magnitude correspond to an activation-energy difference of 30—120 cal./mole. Since the electronic energies of non-vibrating isotopic molecules are necessarily the same, these effects must be vibrational. It was thus assumed that they could be described only in terms of vibrational frequency shifts and could be calculated with the aid of an extension of Bigeleisen's usual treatment³ to secondary isotope effects,⁴ whilst neglecting anharmonicity.

Our aim is to explore whether consideration of differences in mean configuration between isotopic molecules, arising from the anharmonicity of the lowest vibrational levels, could afford a way of dealing with energetic effects of this order of magnitude. In effect, such an approach means substituting for the vibrating molecule a conceptual rigid model, fixed at its mean configuration over the lowest vibrational level, and considering the electron distribution and electronic energy of the slightly different models for isotopic molecules.

The activation energy of carbonium ion formation is difficult to estimate, since it depends critically on the geometry and charge distribution of the transition state. We shall here consider explicitly only the π -electron energy of the *free gaseous* ion, leaving open the question of how closely a given transition state resembles it. Chemically the *solvated* ion is the interesting entity, but at this point only the qualitative statement can be made that the solvation energy should be greater the more concentrated the charge.

Restriction to the π -electron system necessarily implies neglect of inductive effects in the σ -framework, which must be taken as a superimposed additional effect. Inductive electron release from an isolated C-D bond appears to be easier than from C-H,^{5,6} and non-bonding interactions would tend to augment this.⁷ From the strengths of α -deuterated

* Part II, *J.*, 1959, 1974.

¹ Lewis *et al.*, *J. Amer. Chem. Soc.*, 1952, **74**, 6306, and later papers.

² Shiner *et al.*, *ibid.*, 1953, **75**, 2925, and later papers.

³ Bigeleisen, *J. Chem. Phys.*, 1949, **17**, 675.

⁴ Streitwieser, Jagow, Fahey, and Suzuki, *J. Amer. Chem. Soc.*, 1958, **80**, 2326.

⁵ Tiers, *J. Chem. Phys.*, 1958, **29**, 963.

⁶ Elliott and Mason, *Chem. and Ind.*, 1959, 488.

⁷ See Part II for discussion and references.

carboxylic acids and amines we may assess the magnitude of the inductive effect of CD_3 relative to CH_3 to be some 70 cal./mole.⁸

Method of Calculation.—The framework for the treatment of ethyl carbonium ion was set up by Muller and Mulliken.⁹ Since we are here dealing with isovalent hyperconjugation,^{9,10} in which a unit of positive charge is spread over the molecule, our method of calculation differs in several respects from that employed in Parts I and II. The presence of the greater net charges requires a self-consistency procedure, as outlined, for example, by Muller and Mulliken, and, for essentially the same reason, the additional small charges transmitted by induction in the σ -framework and expressed by the coefficient ϵ in Parts I and II can here be reasonably neglected.

Since the parameters which we adopted in Parts I and II differ somewhat from those used by Muller and Mulliken in their calculation for the ethyl carbonium ion, we repeated the calculations for this molecule with our parameters. The value of the free parameter that appears in the self-consistency procedure, ω (which relates the coulomb integral on a given atom to its charge density), was chosen so as to yield a value of the delocalisation energy (vertical hyperconjugation energy) of the ethyl carbonium ion in agreement with that given by Muller and Mulliken.

The iteration procedure was carried out in this and subsequent calculations until self-consistency was reached to within $\pm 0.00005\beta_0$ in the total energy and ± 0.00005 in the charges. This generally required 6–10 iterations for each of the localised and delocalised models.

The results are given in Table I.

TABLE I.

| | | | | | |
|-----------------------|--|----------------------|----------------------|----------------------|--|
| | 1 | 2 | 3 | 4 | |
| | $\text{H}_3\text{C}=\text{C}=\text{H}_2$ | | | | |
| $\omega = 1.30$ | $\delta_1 = -0.45$ | $\delta_2 = 0$ | $\delta_3 = 0$ | $\delta_4 = -0.30$ | |
| | $S_{12} = 0.625$ | $S_{23} = 0.26$ | | | |
| Charges on the atoms: | $\frac{q_1}{0.3465}$ | $\frac{q_2}{0.0546}$ | $\frac{q_3}{0.4302}$ | $\frac{q_4}{0.1687}$ | |
| $E_{\text{mob.}}$ | $= 7\alpha + 10.1795\beta_0$ | | | | |
| $E_{\text{loc.}}$ | $= 7\alpha + 9.4130\beta_0$ | | | | |
| $E_{\text{deloc.}}$ | $= + 0.7665\beta_0$ | | | | |

*The Effect of Configurational Changes.**—We shall assume, as in Part II, that the changes in bond length and angle on going from a methyl group to a deuterated methyl group are in the range:

$$(r_{\text{CH}} - r_{\text{CD}}) = 0.004 - 0.009 \text{ \AA}$$

$$(\chi_{\text{DCD}} - \chi_{\text{HCH}}) = 0.003_s - 0.005 \text{ radian}$$

and we have shown that these correspond to a variation of the overlap integral in the range:

$$\Delta S_{12}/S_{12} = 0.003 - 0.006$$

or

$$\Delta S_{12}/S_0 = 0.008 - 0.016$$

where $S_0 = 0.25$ and $S_{12} = 2.5S_0$.

The change in electropositivity is more difficult to assess accurately. If it is ascribed principally to the $\text{H} \cdots \text{H}$ non-bonding interactions, it depends on the difference in mean $\text{H} \cdots \text{H}$ distance, Δl , which lies in the range:

$$-\Delta l = 0.004 - 0.013 \text{ \AA}.$$

* For notation see Part II.

⁸ Halevi, Nussim, and Ron, unpublished results.

⁹ Muller and Mulliken, *J. Amer. Chem. Soc.*, 1958, **80**, 3489.

¹⁰ Mulliken, *Tetrahedron*, 1959, **5**, 253.

In the case of toluene, the conclusions were not affected by the precise values of the parameters, so rounded median values were taken as follows:

$$\begin{aligned}\Delta S_{12} &= 0.01S_0 \\ \Delta\delta_1 &= 0.02\delta_1\end{aligned}$$

Taking values of S_{12} and δ_1 altered accordingly to represent the effect of changing the mean configuration to that of $D_3=C-C=H_2^+$, we obtain energetic quantities that differ from those of the parent molecule (Table 1) to the extent shown in the first column of Table 2. All energies are in units of β_0 .

In view of the relative sensitivity of isovalent hyperconjugation to variations in the parameters, it was surprising that the effect on the energetic quantities was so small. In the case of toluene it was shown in Part II that varying S_{12} and δ_1 *separately* introduced opposing effects of similar magnitude, and so the calculations were repeated with each of the two parameters varied while the other was held constant. The results appear in columns 2 and 3 of Table 2. Comparison with the data given in Tables 1 and 3 of Part II shows that varying *either* the overlap or the electropositivity operates in the same direction as in toluene, but the effect is larger by a power of ten in the ethyl carbonium ion, corresponding to some 200 cal./mole * in the delocalisation energy.

TABLE 2.

| Column: | 1 | 2 | 3 | 4 |
|---------------------------|--------------------------|--------------------------|-------------------------|------------------|
| | $\Delta S_{12} = 0.0025$ | $\Delta S_{12} = 0.0025$ | $\Delta S_{12} = 0$ | (Sum of |
| | $\Delta\delta_1 = 0.01$ | $\Delta\delta_1 = 0$ | $\Delta\delta_1 = 0.01$ | columns 2 and 3) |
| $\Delta E_{mob.}$ | -0.0035 | +0.0125 | -0.0165 | -0.0040 |
| $\Delta E_{loc.}$ | -0.0045 | +0.0151 | -0.0198 | -0.0047 |
| $\Delta E_{deloc.}$ | -0.0009 | -0.0026 | +0.0033 | +0.0007 |

Since the slight net effect of the combined change arises from a difference between two greater opposed effects, it follows that it was quantitatively unjustified to use rounded median values of the parametric changes, but rather was advisable to evaluate the resultant effect at several assumed configurations of the deuterated molecule, within the estimated range of difference from the parent molecule.

Moreover, the sum of the two separate effects, given in column 4, is in good agreement with the results of the combined variation (column 1). This additivity, which could have been foreseen as a necessary consequence of the superposition of two first-order perturbations, allows us to estimate the net effects at different assumed configurations by evaluating the effect of each factor separately and then combining them.

Variation of Energetic Effects with Configurational Differences.—The variation of S_{12} with bond length and angle was given in equation 5 of Part II:

$$dS_{12}/S_{12} = -0.50dr + 0.34d\chi \quad . \quad . \quad . \quad . \quad . \quad (1)$$

in which r is in Å and χ in radians. The variation of δ_1 with l , the H...H distance, may be calculated by I'Haya's treatment,¹¹ which in our range yields:

$$+ \quad d\delta_1/\delta_1 = 2.47dl \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Using equation 6 of Part II, which expresses the dependence of l on bond length and angle, we obtain:

$$d\delta_1/\delta_1 = 4.04dr + 1.57d\chi \quad . \quad . \quad . \quad . \quad . \quad (3)$$

* The magnitude of β_0 has been variously estimated. It should lie in the range 60–80 kcal./mole.

¹¹ I'Haya, *J. Chem. Phys.*, 1955, **23**, 1165.

From a number of calculations with different values of the parameters δ_1 and S_{12} , we obtain the following dependence of the energetic quantities, in units of β_0 :

$$\left. \begin{aligned} E_{\text{mob.}} &= 7\alpha + 10.1795 + 1.6508\Delta\delta_1 + 5.1264\Delta S_{12} \\ E_{\text{deloc.}} &= 0.7665 - 0.3272\Delta\delta_1 - 0.9024\Delta S_{12} \end{aligned} \right\} \dots (4)$$

In Table 3 are shown the extreme values allowed for Δr and $\Delta\chi$. Although differences in bond length and bond angle between the isotopic variants must be interrelated, we have had to postulate their independence in order to arrive at an estimate of each.¹² Consequently the uncertainties in these quantities must also be regarded as independent, and in principle any of the four combinations of the two limiting values of each are equally acceptable. Of these four, the two combinations which yield the extreme energetic differences are:

$$\begin{aligned} A \Delta r &= -0.009 \text{ \AA}; \quad \Delta\chi = 0.0035 \text{ radian} \\ B \Delta r &= -0.004 \text{ \AA}; \quad \Delta\chi = 0.005 \text{ radian} \end{aligned}$$

These yield the relevant differences in the delocalisation energy, as follows:

$$\begin{aligned} A \Delta E_{\text{deloc.}} &= +0.0015\beta_0 \\ B \Delta E_{\text{deloc.}} &= -0.0006\beta_0 \end{aligned}$$

We see that, within the limits of our uncertainty as to the exact configurational differences between the isotopic molecules, the hyperconjugation energy could be either greater or less in the deuterated molecule. In any event the magnitude of the effect is of the order of 50—100 cal./mole, a significant quantity from the point of view of secondary isotope effects.

TABLE 3.
($S_{12} = 0.625$; $\delta_1 = -0.45$)

| | Δr (\AA) | $\Delta\chi$ (radians) | | |
|--|------------------|------------------------|----------|----------|
| | -0.004 | -0.009 | +0.0035 | +0.0050 |
| Contribution to ΔS_{12} | +0.0012 | +0.00281 | +0.00075 | +0.00106 |
| Contribution to $\Delta\delta_1$ | -0.0078 | -0.0167 | +0.0022 | +0.0033 |

Effect of Normalisation Procedure.—In the calculations discussed so far, we used Muller and Mulliken's normalisation procedure:

$$\sum_{\text{r}}^2 c_{\text{ir}} = 1 \dots (M)$$

In view of the sensitivity of our calculations to small parametric changes, and the consequent ambiguity of the results, we repeated them using Coulson and Chirgwin's more accurate normalisation procedure,¹³ which takes overlap into account:

$$\sum_{\text{r}} \sum_{\text{s}} c_{\text{ir}} s_{\text{rs}} c_{\text{is}} = 1 \dots (C)$$

since it would be even more unsettling were the result to depend critically on the method of calculation employed.

Using the same value of the parameters as before, but altering ω to 1.35 in order to obtain a reasonable value of $E_{\text{deloc.}}$, we found for the reference molecule the values given in Table 4.

The variation of the energetic quantities with the changes in the parameters were here, as usual in units of β_0 :

$$\begin{aligned} E_{\text{mob.}} &= 7\alpha + 10.2436 + 1.6696\Delta\delta_1 + 4.8128\Delta S_{12} \dots (5) \\ E_{\text{deloc.}} &= 0.7384 - 0.2892\Delta\delta_1 - 1.2320\Delta S_{12} \end{aligned}$$

¹² Halevi, *Trans. Faraday Soc.*, 1958, **54**, 1441; see also Part II.
¹³ Coulson and Chirgwin, *Proc. Roy. Soc.*, 1950, *A*, **201**, 196.

TABLE 4.

| | | 1 | 2 | 3 | 4 | | |
|-----------------|--------------------|--|----------------------|----------------------|----------------------|----------------------|--|
| | | $\text{H}_3\equiv\text{C}-\text{C}=\text{H}_2$ | | | | | |
| $\omega = 1.35$ | $\delta_1 = -0.45$ | $\delta_2 = \delta_3 = 0$ | | $\delta_4 = -0.30$ | | | |
| | | $S_{12} = S_{34} = 0.625$ | | $S_{23} = 0.26$ | | | |
| | | Charges on the atoms: | $\frac{q_1}{0.3190}$ | $\frac{q_2}{0.0316}$ | $\frac{q_3}{0.5006}$ | $\frac{q_4}{0.1488}$ | |
| | | $E_{\text{mob.}} = 7\alpha + 10.2436\beta_0$ | | | | | |
| | | $E_{\text{loc.}} = 7\alpha + 9.5052\beta_0$ | | | | | |
| | | $E_{\text{deloc.}} = 0.7384\beta_0$ | | | | | |

Here too the same extreme configurations, *A* and *B*, yielded the limiting effects:

$$A \Delta E_{\text{deloc.}} = -0.0002$$

$$B \Delta E_{\text{deloc.}} = -0.0016$$

Comparison of equations (4) and (5) shows that the two methods of calculation yield the same trends. Normalisation procedure (*C*) favors ΔS_{12} slightly more than does procedure (*M*), so that now the deuterated carbonium ion has less hyperconjugation energy than the normal molecule throughout the range of its assumed mean configuration, the extent of this destabilisation being anything up to some 100 cal./mole.

Effect of Initially Assumed Value of δ_1 .—In all the calculations so far, as in Part II, we have assumed, $\delta_1 = -0.45$. This assumption was based on the qualitative argument that the coulomb integral of a methyl group is greater than that of a methylene group, for which I'Haya¹¹ calculated a value of $\delta_1 = -0.3$. This argument is not compelling, and the difference between the coulomb integrals of the H_3 and the H_2 pseudoatom may be considerably smaller. With this in mind, it seemed advisable to repeat the calculations with $\delta_1 = \delta_4 = -0.3$, to ascertain whether the results are affected by the initial choice of δ_1 . Normalisation was carried out according to (*M*) (see Table 5).

TABLE 5.

| | | 1 | 2 | 3 | 4 | | |
|-----------------|------------------------------|--|----------------------|----------------------|----------------------|----------------------|--|
| | | $\text{H}_3\equiv\text{C}-\text{C}=\text{H}_2$ | | | | | |
| $\omega = 1.35$ | $\delta_1 = \delta_4 = -0.3$ | $\delta_2 = \delta_3 = 0$ | | | | | |
| | | $S_{12} = S_{34} = 0.625$ | | $S_{23} = 0.26$ | | | |
| | | Charges on the atoms: | $\frac{q_1}{0.2953}$ | $\frac{q_2}{0.0800}$ | $\frac{q_3}{0.4453}$ | $\frac{q_4}{0.1794}$ | |
| | | $E_{\text{mob.}} = 7\alpha + 10.5025\beta_0$ | | | | | |
| | | $E_{\text{loc.}} = 7\alpha + 9.7097\beta_0$ | | | | | |
| | | $E_{\text{deloc.}} = 0.7928\beta_0$ | | | | | |

The variation with the parameters was found to be:

$$\left. \begin{aligned} E_{\text{mob.}} &= 7\alpha + 10.5052 + 1.1080\Delta\delta_1 + 5.1840\Delta S_{12} \\ E_{\text{deloc.}} &= 0.7928 - 0.2148\Delta\delta_1 - 0.8640\Delta S_{12} \end{aligned} \right\} \quad \cdot \quad \cdot \quad (6)$$

resulting at the limiting configurations in:

$$A \Delta E_{\text{deloc.}} = +0.0001$$

$$B \Delta E_{\text{deloc.}} = -0.0010$$

Here too, as in the two earlier sets of calculations, the trends are the same. The results favour a decrease in delocalisation energy throughout the range, varying from virtually zero to some 70 cal./mole.

For completeness, we might have calculated yet another set of data, using normalisation procedure (*C*) with an initial value of $\delta_1 = -0.3$. However, it is certain that the trends

would have remained the same, and the results would have indicated hyperconjugative destabilisation of the deuterated ethyl carbonium ion throughout the range of configurational uncertainty, varying from some small value to a maximum of 150 or 200 cal./mole.

Possible Change of S_{23} .—In the original treatment of isotopic variations of mean configuration,¹² the mean values of all symmetry co-ordinates which do not involve displacement of the isotopic atoms were assumed to remain unaltered. This is not strictly true, and the possibility that the anharmonicity of the C–C stretching mode, also totally symmetric, might contract this bond to some extent cannot be excluded. Such a contraction would increase S_{23} and thus affect the energy.

To obtain an upper limit to this bond contraction, the CH_3 and the CD_3 group could be assumed to move as units of mass 15 and 18 respectively, and the decrease in bond length could then be calculated in the usual manner.¹² Taking over Hansen and Dennison's values for the frequency and anharmonicity constant of the C–C stretching mode of ethane,¹⁴ we obtain:

$$\Delta r_{\text{GG}} \leq 0.0004 \text{ \AA}$$

from which, using the dependence of C–C overlap on bond length, we find:

$$\Delta S_{23} \leq 0.0006$$

In a calculation, using normalisation procedure (*M*) and the initial values of the parameters, $\delta_1 = -0.45$, $S_{12} = 0.625$, $S_{23} = 0.26$, increasing S_{23} to this extent lowered the total energy by:

$$\Delta E_{\text{mob.}} \leq 0.0015\beta_0 \simeq 100 \text{ cal./mole}$$

In terms of total π -electron energy, this is a relatively small quantity, but since it is inherent in the method of calculation that a variation in S_{23} cannot effect the energy of the localised model, the entire energetic difference appears in the delocalisation energy, and as such it is considerable.

We see then that the increase in S_{23} on deuteration opposes, in its effect on delocalisation energy, the effect of the accompanying increase in S_{12} . With regard to magnitude, it is difficult to know whether the real effect approximates to the upper limit at all closely, or whether it is no more than a small fraction of it.

In principle, the π -electronic effect of shortening r_{CC} would be opposed by an increase in compression energy, but this is negligible for a contraction of 0.0004 \AA .

Charge Distribution.—From our work on toluene it was clear that the use of the terms "hyperconjugative stabilisation" and "hyperconjugative electron release" as if they were virtually synonymous is unjustified in the case of a neutral conjugated molecule. It is now interesting to see whether this differentiation must still be made in the case of isovalent hyperconjugation, where electron release to an electron-deficient atom would seem to be the principal factor.

TABLE 6.

$\omega = 1.30$; $\delta_1 = -0.45$; $S_{12} = 0.625$; normalisation procedure (*M*).

| | $\Delta\delta_1 = 0.01$ $\Delta S_{12} = 0.0025$ | $\Delta\delta_1 = 0$ $\Delta S_{12} = 0.0025$ | $\Delta\delta_1 = 0.01$ $\Delta S_{12} = 0$ |
|--|---|--|--|
| Δq_1 | +0.0027 | -0.0006 | +0.0033 |
| Δq_2 | -0.0015 | -0.0001 | -0.0014 |
| Δq_3 | -0.0006 | +0.0007 | -0.0013 |
| Δq_4 | -0.0006 | 0.0000 | -0.0006 |
| $\Delta(q_1 + q_2) = -\Delta(q_3 + q_4)$ | +0.0012 | -0.0007 | +0.0019 |

Using the original median values for ΔS_{12} and $\Delta\delta_1$, we show in Table 6 the deviations from the charges given in Table I. We see then that superposition of the separate effects

¹⁴ Hansen and Dennison, *J. Chem. Phys.*, 1952, **20**, 313.

of varying S_{12} and δ_1 yields the same charges on each of the atoms as does the combined variation. It is also evident that electron release from the methyl group as measured by $\Delta(q_1 + q_2)$, is considerably more sensitive to a variation in the electropositivity than to variation in the overlap, although, with this particular choice of parameters, the effect of the two variations on the delocalisation energy is nearly equal (cf. Table 2).

Similar trends, though quantitatively less pronounced, are obtained with normalisation procedure (C).

Discussion.—We see that the delocalisation energy is oppositely affected by the increased effective electropositivity of the D_3 pseudoatom and the increased $D_3 \equiv C$ overlap. The uncertainty of the precise values of the bond length and angle differences and of the best parameters to use prevent an unambiguous conclusion as to the magnitude or even the direction of the net effect. If one may place more credence in the results obtained with more accurate normalisation procedure (C), there is a bias in favour of hyperconjugative *destabilisation* of the deuterated relative to the normal carbonium ion, a destabilisation that may or may not be sufficiently great to override the inductive stabilisation of the deuterated ion.

The difference in charge distribution may become significant when we attempt to consider solvated ions. The solvation energy of the undeuterated ion should be greater, because, other things being equal, the greater electropositivity of D_3 tends to diffuse the charge more effectively, thus presumably reducing the energy of solvation.

To the extent that C-C overlap must be taken into account—and we cannot say at present whether this is a significant factor or a very minor one—it will operate in the opposite direction.

Finally, it should not be forgotten that the present treatment is very approximate. First, there are the usual limitations of the LCAO-MO method itself and the arbitrary element in the choice of parameters. Secondly, in order to arrive at an estimate of the configurational changes we have to regard the totally symmetric bending and stretching modes as completely independent, which cannot be true. Moreover, replacing a molecule by a rigid model can only be justified in terms of an approximation.¹⁵

What can be concluded as regards solvolytic secondary isotope effects is that hyperconjugative as well as inductive effects can be rationalised in terms of configurational differences, and that they are of the same order of magnitude as those found experimentally but are unfortunately quantitatively indeterminate. Further, since the primary assumption that takes the solvated carbonium ion as a model for the activated complex may be a good one in some conditions and a poor one in others, it is evident that the origin of secondary isotope effects in solvolysis is considerably more complex than has been realised up to now, and that it is inadvisable to draw conclusions about their nature from solvolytic experiments alone.

We are much indebted to Dr. Max Wolfsberg for an illuminating discussion of some of the basic assumptions of our treatment.

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[Received, July 2nd, 1959.]

¹⁵ Wolfsberg, Halevi, and Pauncz, unpublished work.