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Electron transfer energies and dipole moments of alkyl halides and amines from an electrostatic model

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Energies of the electron transfer reaction $\text{CH}_3\text{X} + \text{RX}^+ \rightarrow \text{CH}_3\text{X}^+ + \text{RX}$ and dipole moments of molecules RX , where R is an alkyl group and $\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{or } \text{NH}_2$, are calculated for an electrostatic model in which each atom is characterized by a fixed charge and polarizability located at the position of the nucleus. The calculation takes into account the mutual polarization of the atoms in the molecular field. Atom polarizabilities are obtained from previous applications of the atom-dipole interaction model to molecular polarizabilities. Atom charges are assumed to be nonzero only for X and C^α , and these are optimized to fit 13 experimental electron transfer energies from first ionization potentials and 17 gas-phase dipole moments for selected alkyl compounds. Energies of 19 transfer reactions and dipole moments of 29 molecules are calculated, showing satisfactory overall agreement with experiment. The results suggest that the electrostatic interaction of the fixed charges with the polarizable atoms is responsible for the trend toward decreasing ionization potential with increasing size of the R group.

INTRODUCTION

It has long been known that the first ionization potentials of alkyl compounds such as amines, halides, and alcohols, which possess easily ionized lone-pair electrons on the functional group, generally tend toward smaller values as the size of the alkyl group increases.^{1,2} We wish to consider here whether this trend might arise from the electrostatic interaction of the charged group with the polarizable atoms of the molecule. Qualitatively, such an interaction is expected to produce the observed trend. If a polarizability model is quantitatively correct, it would be possible to predict energies of charge transfer reactions in a relatively simple way, without resorting to a detailed quantum mechanical treatment. The model lends itself well to related processes involving large molecules or the interaction of reactant species with a solvent medium.^{3,4}

Our model is essentially the atom-dipole interaction model which has been found in recent years to be valid for the treatment of a variety of optical properties.⁵⁻⁷ The possibility that this model would be suitable for the treatment of charge transfer energies was suggested by a recent study of the $\pi - \pi^*$ absorption spectra of amides; the shift in transition energy with degree of N -alkyl substitution predicted by the atom-dipole interaction model⁶ was in approximate agreement with experiment and with the predictions of Schellman and Nielsen⁸ based on a charge transfer model. The latter authors assumed that the $\pi - \pi^*$ transition involves a charge transfer from the nitrogen atom to a π^* orbital, and used the experimental ionization potentials of alkyl amines to parametrize their theory. The similarity of the results obtained by these two theoretical approaches suggested that the trend in ionization potentials of the amines was itself due to a polarizability interaction.⁸

In the present treatment the electrostatic energy of the molecule is a function of the atom polarizabilities, which are known,^{5,9} and the fixed charges on the atoms, which are not well established. We thus treat the charges as adjustable parameters, but limit the number of parameters by assuming that only certain key atoms

bear charges and, where possible, constrain the charges to give optimal agreement with measured dipole moments. The charge distribution giving rise to the dipole moment consists of two parts in this model, namely, the fixed charges on the atoms and the polarization of the atoms by the molecular field. We will gain information on the relative importance of these two parts.

THEORY

Our model for a molecule⁹ consists of an array of N atoms which interact with each other only by way of the fields of their fixed charges and electric dipole moments induced by the molecular field. Atom i is characterized by its charge q_i and dipole polarizability α_i located at the position of the nucleus \mathbf{r}_i . In this model the atoms do not possess permanent multipole moments, higher multipole polarizabilities, or hyperpolarizabilities, all of which would contribute to the electrostatic energy but would burden the theory with inaccessible parameters. The atoms will be regarded as isotropic in our numerical calculations, though the equations apply to the anisotropic case as well. Intermolecular interactions are not considered.

The electrostatic energy of the molecule is calculated as the work required to assemble the atoms in their final positions from an initial state of infinite separation. Böttcher *et al.*¹⁰ have derived expressions for the electrostatic energies of various systems of charges; by following essentially their arguments (see Appendix) we obtain the following expression for the work W performed on the system in the assembly process, including both the work required to polarize each atom and that required to move the atoms successively to their final positions:

$$W = \frac{1}{2} \sum_i \sum_j' q_i \phi_{ij}, \quad (1)$$

where the primed sum omits the term $j=i$ and ϕ_{ij} is the electrostatic potential at atom i due to the charge q_j and induced dipole moment μ_j on atom j , given

$$\phi_{ij} = q_j / r_{ji} + \mu_j \cdot \mathbf{r}_{ji} / r_{ji}^3, \quad (2)$$

where $\mathbf{r}_{ji} = \mathbf{r}_i - \mathbf{r}_j$. The dipole moments are obtained by solving the matrix equation⁹

$$\mathbf{A}\boldsymbol{\mu} = \mathbf{F}, \quad (3)$$

where \mathbf{A} is the $3N \times 3N$ interaction matrix,⁹ $\boldsymbol{\mu}$ is a column vector of the atom dipole moments, and \mathbf{F} is a column vector of the fields \mathbf{F}_i at atom i due to the fixed charges on other atoms:

$$\mathbf{F}_i = \sum_j' q_j \mathbf{r}_{ji} / r_{ji}^3. \quad (4)$$

The solution to Eq. (3) is obtained in the form $\boldsymbol{\mu} = \mathbf{A}^{-1}\mathbf{F}$. The permanent molecular dipole moment is given by

$$\boldsymbol{\mu}_{\text{mol}} = \sum_i (q_i \mathbf{r}_i + \boldsymbol{\mu}_i). \quad (5)$$

We wish to calculate the reversible work performed on the system in the electron transfer process



where R is an alkyl group and X = Cl, Br, I, or NH₂. A necessary condition for the work to be equal to ΔW as calculated above is that the set of atoms which make up the reactants be identical in charge and polarizability to the set of atoms which make up the products, so that the reference state (isolated atoms) will be the same on both sides of the equation. If this condition did not hold, there would be contributions from the work required to transfer charge between dissimilar atoms, and our model provides no basis for calculating such contributions.

Regarding the thermodynamic function corresponding to ΔW , we assume that the substances are ideal gases in their standard states and that the reaction occurs at constant temperature and pressure. Thus $\Delta W = \Delta G^\circ$, the change in standard Gibbs energy. We also assume for the present that all molecules have rigid structures. Then, for our model, $\Delta G^\circ = \Delta A^\circ = \Delta H^\circ = \Delta U^\circ$, since the volume is constant and the electrostatic work is independent of temperature ($\partial \Delta G^\circ / \partial T = -\Delta S^\circ = 0$). Thus we will call ΔW simply the energy of electron transfer. A similar identity of thermodynamic functions appears to hold in reality, as the ionization potentials of gases measured by photoelectron spectroscopy are usually independent of temperature and pressure.¹¹ Thus the difference between appropriate ionization potentials can be taken as a measure of any of the standard state thermodynamic energy functions for Reaction (6).

METHODS

A central feature of this study is the choice of atom charges, for which suitable values are not available from other sources. We sought to test the model by finding a limited set of charges which give an optimum fit to experimental electron transfer energies and dipole moments of neutral molecules. To keep the charge set as small as possible and to satisfy the constraint of identity of charges in reactants and products, we assumed that the only atoms bearing charges are C^α, halogen, N, and amino H, and that these charges are identical in homologous molecules in the same ionization state. Since the total molecular charge is fixed at 0 or +1, there are two adjustable charge parameters for each

homologous series of halides (one parameter for each charge form) and four parameters for the series of amines. The values were optimized to fit three electron transfer energies and four dipole moments for each halide series and to fit four transfer energies and five dipole moments for the amine series. The methyl, ethyl, *n*-propyl, and *n*-butyl compounds in all series were included in the optimization; in addition, *i*-propylamine was included in the optimization for the amine series. Calculations for branched alkyl halides using the charges optimized for the unbranched species are included in the results.

A nonlinear least-squares method was used to determine the atom charges which minimize the unweighted sum of squares of fractional deviations between calculated and experimental quantities (transfer energies and dipole moments). The IMSL subroutine ZXSSQ served this purpose.¹² A single set of optimum charges was located regardless of the choice of initial trial charges, which covered a range of ± 1 a.u. Standard deviations of the charges were estimated as described elsewhere.⁶

Molecular structures were generated from bond lengths, bond angles, and torsion angles using subroutine ATCOOR.¹³ The bond lengths (Å) in the neutral species were¹⁴: CC 1.537 (1.550 for C^αC^β in halides), CH 1.096 (1.093 in methylamine), CCl 1.779, CBr 1.938, CI 2.207, CN 1.472 (1.474 for methylamine), NH 1.012 (1.013 for methylamine). The bond angles (deg) in the neutral species were¹⁴: CClI 110.5, CClBr 110.5, CCI 112.02, CCC 110.0, CCN 110.0, CCH 109.471, NCH 109.471, HCH 109.471, CNH 112.20, HNH 105.80. For the methyl halides the slightly different bond parameters of Costain¹⁵ were used. All bond angles in the *t*-butyl group were set at 109.471°. The cations of alkyl halides were assumed to have the same structures as the neutral species. The alkyl amine cations were assumed to have planar structures about the nitrogen¹⁶ with angle CNH = 121.5° and CN and NH distances reduced by 0.017 and 0.013 Å, respectively, corresponding to the difference in single bond distances between propane and propylene,¹⁴ which have a similar difference in orbital hybridization. Staggered conformations about the single bonds were assumed. The C^β-C^γ bond in the *n*-butyl group was placed in the *trans* form throughout, while the C^α-C^β bonds in the *n*-propyl, *n*-butyl, *i*-butyl, and *s*-butyl groups were placed in both *trans* and *gauche* conformations with respect to X in separate calculations. Amino hydrogens in both neutral and cation forms were placed symmetrically with respect to C^β (or methyl H in methylamine) so as to maximize staggering about C-N; these conformations were those found to have minimum energies in preliminary calculations which included both electrostatic and nonbonded energies.³

Atom polarizabilities were taken as the values optimized to fit molecular polarizabilities at the Na D wavelength by means of the atom dipole interaction model^{5,9} (Å³): C 0.878, N 0.618, Cl 1.91, Br 2.88, I 4.69, H(alkyl) 0.135, H(amine) 0.155. It might be supposed that the loss of an electron by ionization re-

sults in a loss of polarizability by the atoms affected. To illustrate the effect of such a loss, some of the calculations were carried out with reduced values of the polarizabilities of ionized halogen or nitrogen, the atoms most strongly affected by the ionization of the molecule. A reduction by 1/7 was assumed for halogens and 1/5 for nitrogen, corresponding roughly to the fraction of valence electrons lost on ionization.

Experimental electron transfer energies were obtained from available first ionization potentials determined by photoelectron spectra of the gaseous substances.¹⁷⁻²⁰ A preliminary study on amines³ based on earlier ionization potentials from photoionization measurements²¹ gave charges which differed in some respects from those reported here, but the predicted properties were similar. The photoelectron spectra normally give vertical ionization potentials which, for lone-pair electrons, correspond to transitions between the ground vibrational levels²²; it is thus reasonable to suppose that the energies correspond to isothermal processes. Where the first ionization potential is split due to spin-orbit coupling,¹⁷⁻²⁰ we have taken the lowest energy component. Uncertainties in electron transfer energies are in the range 1-4 kJ/mol, judging from stated uncertainties of individual measurements and the reproducibility of measurements from various sources.

The experimental dipole moments of all compounds were obtained as averages of all values in McClellan's tables^{23,24} for particular conditions (gas phase where available; otherwise solution values in a particular solvent). Standard deviations are typically ± 0.1 D.

Calculations were carried out on an Itel AS/6 computer using double precision arithmetic.

RESULTS

Table I shows the optimized atom charges found for each homologous series of compounds. The optimizations were carried out under three sets of assumptions, designated I, II, III, concerning the $C^\alpha-C^\beta$ conformation and the polarizability of halogen or nitrogen. The differences among the charge sets are of the order of the estimated standard deviations, which are relatively small for the halides but large for the amines. A large standard deviation means only that the experimental data are fitted about equally well by a broad range of the charge involved, and does not reflect on the quality of the fit.

Table II shows the energies of Reaction (6) calculated for each of the charge sets and conditions in Table I. Results are included for some branched alkyl halides, which were not included in the optimization of charges (data in parentheses). The calculations show little dependence on the charge set and are mostly within the range of experimental uncertainty (1-4 kJ/mol); exceptions are the *i*-propyl and *t*-butyl bromides and iodides, which show discrepancies of 6-18 kJ/mol. The similarity of results for the various charge sets implies that assumptions regarding conformation and the effect of ionization on atom polarizability are unimportant.

Table III shows the dipole moments calculated for neutral RX molecules with each of the charge sets and conditions in Table I. Results are given for some branched alkyl halides, which were not included in the optimization of charges (data in parentheses). Most of the deviations from experimental data are within 0.2 D, and are thus comparable to experimental uncertainties; the main exception is methyl iodide, for which the calculated

TABLE I. Optimized atom charges (a. u.) for molecules RX.

Molecular state	Atom ^a	I ^b	II ^c	III ^d
Neutral	Cl	-0.81 \pm 0.05	-0.81 \pm 0.05	-0.97 \pm 0.04
	C ^{Cl}	0.81 \pm 0.05	0.81 \pm 0.05	0.97 \pm 0.04
	Br	-0.64 \pm 0.03	-0.64 \pm 0.03	-0.74 \pm 0.03
	C ^{Br}	0.64 \pm 0.03	0.64 \pm 0.03	0.74 \pm 0.03
	I	-0.39 \pm 0.04	-0.39 \pm 0.04	-0.44 \pm 0.04
	C ^I	0.39 \pm 0.04	0.39 \pm 0.04	0.44 \pm 0.04
	N	-0.24 \pm 0.05	-0.24 \pm 0.05	-0.32 \pm 0.05
	H ^N	0.25 \pm 0.19	0.265 \pm 0.20	0.135 \pm 0.14
	C ^N	-0.26 \pm 0.23	-0.29 \pm 0.24	0.05 \pm 0.19
Cation	Cl	1.09 \pm 0.09	0.98 \pm 0.07	1.06 \pm 0.07
	C ^{Cl}	-0.09 \pm 0.09	0.02 \pm 0.07	-0.06 \pm 0.07
	Br	1.03 \pm 0.05	0.96 \pm 0.04	0.98 \pm 0.05
	C ^{Br}	-0.03 \pm 0.05	0.04 \pm 0.04	0.02 \pm 0.05
	I	0.95 \pm 0.04	0.95 \pm 0.04	0.96 \pm 0.04
	C ^I	0.05 \pm 0.04	0.05 \pm 0.04	0.04 \pm 0.04
	N	1.78 \pm 0.16	0.58 \pm 0.52	1.03 \pm 0.29
	H ^N	-0.005 \pm 0.15	0.535 \pm 0.78	-0.30 \pm 0.11
	C ^N	-0.77 \pm 0.29	-0.65 \pm 0.27	0.57 \pm 0.35

^aAtom to which C or H is attached is designated by superscript.

^bTorsion angle $\theta(X, C^\alpha, C^\beta, C^\gamma) = 180^\circ$.

^cSame as I but with halogen polarizability reduced by 1/7 or nitrogen polarizability reduced by 1/5 for cations.

^dTorsion angle $\theta(X, C^\alpha, C^\beta, C^\gamma) = 60^\circ$.

TABLE II. Energies (kJ/mol) of the electron transfer reaction $\text{CH}_3\text{X} + \text{RX}^+ \rightarrow \text{CH}_3\text{X}^+ + \text{RX}$.

X	R	Calc. ^a			Exptl. ^b
		I	II	III	
Cl	Ethyl	26.8	26.6	26.5	27 ^c
	<i>n</i> -Propyl	38.5	38.6	36.9	40 ^c
	<i>n</i> -Butyl	45.0	45.1	47.9	43 ^c
Br	Ethyl	22.1	22.1	23.1	22 ^d
	<i>n</i> -Propyl	33.3	33.4	30.6	34 ^d
	<i>i</i> -Propyl	32.3	32.7	33.8	(40) ^d
	<i>n</i> -Butyl	39.4	39.3	40.3	39 ^d
	<i>i</i> -Butyl	37.1	36.6	36.5 ^e	(41) ^d
	<i>t</i> -Butyl	36.5	37.5	38.3	(56) ^d
I	Ethyl	17.4	17.5	18.9	18 ^f
	<i>n</i> -Propyl	27.1	27.0	24.2	27 ^f
	<i>i</i> -Propyl	25.3	25.0	26.3	(35) ^f
	<i>n</i> -Butyl	32.0	31.8	31.7	30 ^f
	<i>i</i> -Butyl	29.5	29.1	29.0 ^e	(33) ^f
	<i>t</i> -Butyl	27.3	27.0	27.7	(48) ^f
NH ₂	Ethyl	14.9	14.9	15.2	14 ^g
	<i>n</i> -Propyl	18.7	19.1	17.9	19 ^g
	<i>i</i> -Propyl	27.2	26.0	27.1	32 ^g
	<i>n</i> -Butyl	24.4	24.5	24.1	23 ^g

^aRoman numerals denote charge sets and conditions defined in Table I.

^bParentheses indicate data not used in the optimization of charges.

^cReference 17.

^dReference 18.

^eStaggered conformation with a plane of symmetry.

^fReference 19.

^gReference 20.

moment is too small by 0.5–0.6 D. Charge sets I and II give virtually identical results, indicating that the assumptions about the effect of ionization on atom polarizability are not crucial. Sets I and III are similar, but occasionally differ by 0.3–0.4 D. In cases where the compounds involved have the same conformation in both sets (e.g., *i*-propyl and *t*-butyl halides), this difference is due solely to the difference in charges.

The calculated moments include contributions from both the fixed charges and the induced atom dipole moments, both of which are significant. The moments due to fixed charges alone are, for charge set I: chlorides 6.9, bromides 6.0, iodides 4.2, amines 3.0 D. The much smaller values of the total moments (Table III) come about because the major atom polarizations oppose the fixed charge moments. The most strongly polarized atoms are those adjacent to charged atoms (X, C^α, C^β); however, the polarization of other atoms is not negligible (e.g., 0.16 D on C^δ in *n*-butyl chloride), and accounts for the variation in dipole moments within a homologous series.

DISCUSSION

The calculated energies for Reaction (6) and dipole moments of neutral molecules show satisfactory agreement with experiment in most cases. The model shows the trend of increasing energy of electron transfer with

increasing polarizability of the R group, a finding that was expected from the consideration that a polarizable group would act to stabilize the charged form. Transfer energies for branched R groups in the halides are calculated to be within 4 kJ/mol of those for the unbranched form, indicating that the total polarizability of the R group is more significant in this model than the details of its arrangement around the ionizable group. This behavior is not, however, borne out by the experimental data, which show trends toward increasing transfer energy with increasing degree of branching above the level of uncertainty (± 4 kJ/mol).

The model thus reproduces the major experimental observations, though not all the details. While this success must be attributed in part to the fact that the atom charges were optimized for a best fit, the fact that a good fit was obtained suggests that the model corresponds to reality in some degree. Whether the electrostatic effect assumed in the model actually dominates

TABLE III. Dipole moments (D) of neutral molecules RX.

X	R	Calc. ^a			Exptl. ^b
		I	II	III	
Cl	Methyl	1.45	1.45	1.74	1.87
	Ethyl	1.89	1.89	2.26	2.04
	<i>n</i> -Propyl	2.24	2.24	1.99	2.02
	<i>i</i> -Propyl	2.18	2.18	2.61	(2.17)
	<i>n</i> -Butyl	2.33	2.33	2.02	2.10
	<i>i</i> -Butyl	1.97	1.97	1.69 ^c	(2.06)
	<i>s</i> -Butyl	2.44	2.44	2.27 ^d	(2.14)
	<i>t</i> -Butyl	2.36	2.36	2.83	(2.14)
Br	Methyl	1.50	1.50	1.72	1.81
	Ethyl	1.93	1.93	2.21	1.96
	<i>n</i> -Propyl	2.23	2.23	1.98	2.12
	<i>i</i> -Propyl	2.14	2.14	2.45	(2.21)
	<i>n</i> -Butyl	2.33	2.33	2.03	2.14
	<i>i</i> -Butyl	1.97	1.97	1.71 ^c	(1.99) ^e
	<i>s</i> -Butyl	2.36	2.36	2.14 ^d	(2.22)
	<i>t</i> -Butyl	2.23	2.23	2.55	(2.21)
I	Methyl	0.99	0.99	1.11	1.64
	Ethyl	1.88	1.88	2.11	1.80
	<i>n</i> -Propyl	2.12	2.12	1.95	1.89
	<i>i</i> -Propyl	2.02	2.02	2.27	(2.09) ^f
	<i>n</i> -Butyl	2.22	2.22	2.02	2.10
	<i>i</i> -Butyl	1.91	1.91	1.75 ^c	(1.94) ^f
	<i>s</i> -Butyl	2.20	2.20	2.06 ^d	(2.12) ^f
	<i>t</i> -Butyl	2.01	2.00	2.26	(2.13)
NH ₂	Methyl	1.16	1.18	1.03	1.29
	Ethyl	1.16	1.17	1.17	1.11
	<i>n</i> -Propyl	1.19	1.19	1.13	1.18
	<i>i</i> -Propyl	0.86	0.85	1.12	1.20 ^g
	<i>n</i> -Butyl	1.22	1.22	1.17	1.00

^aRoman numerals denote charge sets and conditions defined in Table I.

^bFrom McClellan's tables (Refs. 23 and 24). Average gas phase values except as noted. Parentheses indicate data not used in the optimization of charges.

^cStaggered conformation with a plane of symmetry.

^dTorsion angle $\theta(\text{C}, \text{C}, \text{C}, \text{C}) = 180^\circ$ assumed.

^eMeasured in benzene (Ref. 23).

^fMeasured in CCl₄ (Refs. 23 and 24).

^gMeasured in heptane (Ref. 24).

the transfer energies of real molecules depends on whether the optimized atom charges are physically realistic.

The atom charges satisfy certain conditions which support their validity: (i) they lead to correct dipole moments of neutral species, which are the only direct measurements of charge distribution; (ii) the charge on the halogen in neutral halides is negative, and increasingly so with increasing electronegativity; (iii) among the cations, most of the positive charge is assigned to the atom which loses a lone-pair electron; and (iv) among the neutral species the charges are fractions of an atomic unit, as expected for covalently bonded atoms. It is encouraging that these conditions are met even under the simplifying assumption of zero charge on all alkyl group atoms except C α .

A more quantitative test of the charges is difficult to achieve. The molecular orbital calculations of Hehre and Pople²⁵ for neutral methylamine gave the following charges: N -0.40, H^N 0.15, C 0.11 a.u. These are within the range of uncertainty of the values in charge set III. Similar calculations on alkyl halides by Armstrong *et al.*²⁶ and by Boca *et al.*²⁷ gave charges Cl -0.26, Br -0.11 a.u., which are much smaller than the values in Table I. The same calculations gave charges of 0.1 a.u. or less to C α , the remainder of the positive charge being distributed among other atoms of the alkyl group. All of these atom charges are based on the populations of basis set atomic orbitals. Because of orbital overlap, these populations do not necessarily give a measure of the charge in a region that might be defined as belonging to one atom; there is, therefore, no direct relation between these charges and those appropriate to our model. Wiberg²⁸ has compared "population" charges with charges calculated by integrating the molecular orbital charge density within boundaries assigned to an atom. His integrated charges for atoms in various organic molecules differ substantially from population charges and depend strongly on the location of the boundary between bonded atoms. Thus there are severe difficulties in obtaining charges appropriate to our model from molecular orbital theory. Our assumption that the charge assignable to an atom is localized at a point may require that somewhat artificial charges be assigned to atoms in order to reproduce the effects of the true charge distribution. The same difficulty exists in regard to our atom polarizabilities, yet the same polarizabilities have been found to be valid for the prediction of a variety of properties when treated according to the same model.⁴⁻⁶

The present study is an attempt to identify a particular electrostatic interaction as the dominant effect in producing the trends in ionization potentials. The same effect would be implicit in an accurate quantum mechanical treatment of the energy, but its role is likely to be obscured by the complexity of the problem. Semiempirical molecular orbital methods²⁹⁻³¹ have, in fact, proven capable of predicting trends in ionization potentials in various series of alkyl compounds, including those studied here. In such calculations the interactions responsible for the trends are reflected in some way in

the parameters of the Hamiltonian matrix, but because of the empirical origin of these parameters the nature of the physical forces is not revealed. Our results suggest that the mutual polarization of atoms by their fixed charges is the dominant effect.

Postscript. The referee has called our attention to the related studies of Benson and Luria,³² who treated heats of formation, heats of isomerization, and dipole moments of hydrocarbons by means of an electrostatic model involving Coulombic interactions between fixed charges located at the atomic nuclei. In contrast to the present findings, these authors conclude that the contribution of induced dipoles to the energies is negligible, while the trend in electron transfer energies in our model is due entirely to induced dipole contributions. This difference in conclusions may well arise from differences in mathematical methods; we have solved the interaction problem in a way that includes the effects of induced moments as well as fixed charges on local fields, while Benson and Luria do not appear to have done so.

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APPENDIX

The derivation of Eq. (1) will be given here. Initially the atoms are at infinite separation in empty space. The first step in assembling the molecule is to polarize each atom i to its final dipole moment μ_i as it exists in the assembled molecule. The work performed on the atoms in this step is

$$W_1 = \frac{1}{2} \sum_i \sum_j' \mu_i \cdot \mathbf{E}_{ij}, \quad (\text{A1})$$

where \mathbf{E}_{ij} is the field at atom i due to the charge and dipole on atom j in the final molecule. The second step is to bring the atoms successively to their final positions in the molecule. If the atoms are introduced in the order 1, 2, ..., N , the work performed in this step is

$$W_2 = \sum_{i=2}^N \sum_{j=1}^{i-1} (q_i \phi_{ij} - \mu_i \cdot \mathbf{E}_{ij}). \quad (\text{A2})$$

If the atoms are introduced in the order $N, N-1, \dots, 1$, the work for this step is unchanged, but the sums in (A2) are over $i=1, \dots, N-1$ and $j=i+1, \dots, N$. By adding the resulting expression to Eq. (A2), one obtains

$$W_2 = \frac{1}{2} \sum_i \sum_j' (q_i \phi_{ij} - \mu_i \cdot \mathbf{E}_{ij}). \quad (\text{A3})$$

Equation (1) is then obtained by setting $W = W_1 + W_2$. Böttcher *et al.*¹⁰ derived a formally similar equation [Eq. (3.22), Ref. 10] for the energy of an array of fixed charges, omitting the contribution of induced dipoles. Because of the cancellation of the terms $\mu_i \cdot \mathbf{E}_{ij}$ in Eqs. (A1) and (A3), the dipoles contribute only through the potentials [Eq. (2)]. According to (1) and (2), the total energy contains charge-charge and charge-dipole terms, but no dipole-dipole terms.

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