[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF UTAH]

α-Hydrogen Bonding—A Theory of the Baker–Nathan Effect

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The interactions between 1,3-atoms in complex molecules have been examined, particularly for the case in which one of the atoms is hydrogen. The added stabilization which results from such interactions is approximately proportional to the number of hydrogen atoms in a 1,3-relationship with a π-orbital. The name "α-hydrogen bonding" is suggested for this added stabilization and the calculations suggest that it is large enough to account for a substantial fraction of the Baker–Nathan effect. Calculations were carried out by the empirical L.C.A.O.—M.O. method and yield semi-quantitative agreement with empirical estimates of the Baker–Nathan effect.

There is now a considerable body of evidence indicating that the introduction of a hydrogen atom in a position one atom removed from an unsaturated system produces a stabilization beyond that to be expected from an inductive effect.[3] Stabilization of an unsaturated species by α-hydrogen atoms was first noted by Baker and Nathan.[4] While there is probably no single piece of evidence which cannot, somehow, be explained in other ways[5] the data seem most simply and convincingly explained if it is assumed that a hydrogen atom one atom removed from an unsaturated system lowers the potential energy of the molecule containing it.

Mulliken and co-workers[3e,6] have developed a theory in which the three hydrogens of a methyl group or the two hydrogens of a methylene group are treated as a united atom. The stabilization is then obtained by a sort of second-order conjugation to which Mulliken gave the name "hyperconjugation."[6] Hyperconjugation reproduces the broad features of the Baker–Nathan effect reasonably well but there is no reason to assume that this is the only possible cause of the Baker–Nathan effect.[7]

The present paper develops the idea that a reasonably small, but non-zero resonance integral, $\int \psi_1 H \psi_3 \, d\tau$, for the hydrogen 1s orbital with an orbital one atom removed from it will account for the Baker–Nathan effect. The theory is developed in terms of the simple, empirical, linear combination of atomic orbitals–molecular orbitals (L.C.A.O.-M.O.) method to facilitate both the present calculations and future applications.

Theory

In the usual quantum mechanical calculations on complex molecules interactions between non-bonded atoms are equated to zero.[6,8] Phenomena such as barriers to rotation about single bonds,[9] rotational isomerism,[9] and optical rotation,[10] all of which depend on the interactions between non-bonded atoms, provide direct evidence that this is not exactly true.

That this interaction leads to a very substantial stabilization, neglecting nuclear repulsions, is indicated by the stability of H_3^+[11] and the small activation energy for the reaction $H + H_2$.[12]

The transition state for the reaction $H + H_2$ and the normal state for H_3^+ are both characterized by the fact that an additional nucleus is brought within bonding distance of a stable, saturated, hydrogen molecule. The transition state would be quite a stable molecule were it not for the nuclear repulsion. In spite of the nuclear repulsion H_3^+ is very stable. In the present paper nuclear repulsion is neglected because it has been "paid for," and the internuclear distances fixed, by the σ-bond framework. Cases which involve changes in internuclear distances will not be treated.

The problem, then, reduces itself to the assignment of appropriate values to the resonance integrals for orbitals on non-adjacent atoms. These are thought to be particularly significant when one of these atoms is hydrogen, because of the non-directional character of the hydrogen 1s orbital. The present theory utilizes the Morse function[13] and spectroscopic data to evaluate the needed 1,3-resonance integrals involving the hydrogen atom, and otherwise uses the usual approximations of the L.C.A.O.—M.O. method.

A simple example of an application to a carbonium ion will be discussed as an illustration. To the L.C.A.O.—M.O. approximation the secular equation for the ion H_1-C_2-C_3^+ can be written

$$0 = \begin{vmatrix} (H_{11} - S_{11}E) \ldots (H_{15} - S_{15}E) \\ \ldots\ldots \\ (H_{51} - S_{51}E) \ldots (H_{55} - S_{55}E) \end{vmatrix} \qquad (1)$$

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(3) (a) J. W. Baker, "Hyperconjugation," Oxford at the Clarendon Press, Oxford, 1952; (b) R. W. Taft and M. M. Kreevoy, THIS JOURNAL, **79**, 4011 (1957); (c) E. A. Halonen, *Acta Chem. Scand.*, **9**, 1636 (1955); (d) M. M. Kreevoy and R. W. Taft, Jr., THIS JOURNAL, **77**, 5590 (1955); (e) A. Lofthus, *ibid.*, **79**, 24 (1957). Other examples too numerous to mention may be found by reference to these papers or by perusal of the literature.

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

(5) (a) M. J. S. Dewar and R. Pettit, *ibid.*, 1625 (1954); (b) A. Burawoy and E. Spinner, *ibid.*, 3752 (1954); (c) W. M. Schubert and W. A. Sweeney, *J. Org. Chem.*, **21**, 119 (1956).

(6) R. A. Mulliken, C. A. Rieke and W. G. Brown, THIS JOURNAL, **63**, 41 (1941); reference to other pertinent work by Mulliken may be found in this paper.

(7) In this paper the experimentally observed effect will be called the Baker–Nathan effect, the effect predicted by the Mulliken picture will be called the hyperconjugation effect, and the effect predicted by the present model will be called the α-hydrogen bonding effect.

(8) (a) E. Huckel, *Z. Physik*, **70**, 204 (1931); (b) **76**, 310 (1932); (c) **76**, 628 (1932); (d) J. E. Lennard-Jones and C. A. Coulson, *Trans. Faraday Soc.*, **35**, 811 (1939).

(9) S. Mizushima, "Structure of Molecules and Internal Rotation," Academic Press, New York, N. Y., 1954.

(10) (a) E. U. Condon, *Rev. Modern Phys.*, **9**, 432 (1937); (b) W. J. Kauzmann, J. E. Walter and H. Eyring, *Chem. Revs.*, **26**, 339 (1940).

(11) J. O. Hirschfelder, *J. Chem. Phys.*, **6**, 795 (1938).

(12) S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., New York, N. Y., 1941, p. 107.

(13) G. Herzberg, "Molecular Spectra and Molecular Structure I. Spectra of Diatomic Molecules," D. Van Nostrand Co., Princeton, N. J., 1950, p. 101.

where $H_{mn} = \int \psi_m H \psi_n d\tau$ and $S_{mn} = \int \psi_m \psi_n d\tau$, and

$$\begin{aligned} \psi_1 &= \mathrm{H_1\ 1s\ orbital} \\ \psi_2 &= \mathrm{C_2\ 2sp^3\ orbital} \\ \psi_3 &= \mathrm{C_2\ 2sp^3\ orbital} \\ \psi_4 &= \mathrm{C_3\ 2sp^2\ orbital} \\ \psi_5 &= \mathrm{C_3\ 2p\ orbital} \end{aligned} \qquad (2)$$

Neglecting overlap, eq. 1 immediately becomes

$$0 = \begin{vmatrix} (H_{11} - S_{11}E) & H_{12}\ldots & H_{15} \\ H_{21} & (H_{22} - S_{22}E)\ldots & H_{25} \\ \ldots\ldots & & \\ H_{51} & H_{52}\ldots & (H_{55} - S_{55}E) \end{vmatrix} \qquad (3)$$

At this point all H_{mn} where ψ_m and ψ_n are bonding to each other are assumed to be equal and abbreviated as β. All other H_{mn}'s are set equal to zero except that $H_{15} = H_{51}$ is set equal to $^1/_4\,\beta$, this latter being the new feature of the present work.

It can be seen that these assignments are not unreasonable. Most covalent bonds in organic compounds are of about the same strength, being of the order of magnitude of 50 to 100 kcal./mole so that H_{mn} values for bonding orbitals would be expected to be of the same order of magnitude. The Morse function[13] and spectroscopic properties[14] of the molecule C–H indicate that it would retain about one-fourth of its bond strength with an internuclear distance equal to that separating H_1 from C_3.

For comparison H_{15} also has been estimated from the equation[15]

$$H_{15} = \beta\,\frac{A_{15}I_{15}S_{15}/(1 + S_{15})}{AIS/(1 + S)} \qquad (4)$$

where quantities marked with the subscript 15 refer to interactions between ψ_1 and ψ_5 and others refer to the π-bond of an aromatic carbon–carbon bond. Equation 4 is based on the assumption that the exchange integral is a nearly constant fraction of the bond energy.[16] The parameters A were those of Mulliken,[16] and the mean ionization potentials I were assumed to be those of the atoms with the appropriate hybridization. Values of S for Slater atomic orbitals were obtained by interpolating from the tables of Mulliken, Rieke, Orloff and Orloff.[17] The angular distortion of the H_1C_3 bond was taken into account by multiplying S_{15} by the cosine of the angle made by the symmetry axis of ψ_5 and the line H_1C_3. Equation 4 gives $H_{15} = 0.3\beta$, in respectable agreement with the value estimated above from spectroscopic data.[18] Following Mulliken,[6] all H_{mm}'s are set equal. This choice does not greatly affect the final results[6] and simplifies the calculations. The H_{mn}'s which were set equal to zero probably also have non-zero values, but it is assumed that these values do not change drastically on going from a saturated to an unsaturated molecule, so that they do not appreciably affect the properties in which we are interested. In spite of these arguments, it must be stated that the choice of values for H_{mn} is somewhat arbitrary and the justification of the values chosen must come principally from the results obtained.

With these approximations, eq. 3 can be rewritten and rearranged to give

$$0 = \begin{vmatrix} -E & \beta & 0 & 0 & 0 \\ \beta & -E & 0 & 0 & 0 \\ 0 & 0 & -E & \beta & 0 \\ 0 & 0 & \beta & -E & ^1/_4\beta \\ 0 & 0 & 0 & ^1/_4\beta & -E \end{vmatrix} \qquad (5)$$

That is to say, the carbon–carbon bond is considered isolated from the rest of the system and need not be considered any further. Equations such as 6, which follows directly from 5, provide the starting point for the rest of the work described in this paper.

$$0 = \begin{vmatrix} -E & \beta & 0 \\ \beta & -E & ^1/_4\beta \\ 0 & ^1/_4\beta & -E \end{vmatrix} \qquad (6)$$

From this example, it is clear that the added stabilization which α-hydrogen bonding confers on molecules is introduced by enlarging the volume in which the electrons are free to move. Thus α-hydrogen bonding is responsible for the two $^1/_4\,\beta$ terms in eq. 5, which permit the electrons of the C–H bond to be delocalized into the unsaturated system, represented in this case by the single $-E$ term in the third line. It can be seen that α-hydrogen bonding modifies the secular determinant in much the same way as hyperconjugation, so the two can be expected to predict the same sort of effects, but to a first approximation α-hydrogen bonding permits each C–H bond to exert an effect independently, while hyperconjugation requires the CH_2 or CH_3 group to act as a unit.[6] As a next approximation it must be recognized that the α-hydrogen bonding effect approaches zero as the hydrogen atom approaches the nodal plane of the carbon 2p orbital, while the effect will reach a maximum when the hydrogen atom is in the plane perpendicular to the nodal plane of the carbon 2p orbital. Thus the first hydrogen will have the largest effect, since it can occupy the most favorable position and successive hydrogens will have successively smaller effects, since the geometry must be a compromise. On the other hand there will be a leveling of the effect per hydrogen atom by rotation about carbon–carbon single bonds.

If a carbon atom were present in place of H_1 (in the example given above) its orbitals would be so strongly directed at the atoms to which it would be bonded that they would be relatively ineffective in bonding to the C_3 orbitals. Using the methods described above to calculate the overlap and then the resonance integrals it is found that H_{15}' is $^3/_4$ of H_{15}. The delocalization energy obtained by considering C_1C_3 interactions in $C_1–C_2–C_3^+$ (to which H_{15}' pertains) is only about half of that obtained by considering H_1C_3 interactions in $H_1–C_2–C_3^+$. This is clearly a matter of degree rather than of kind, but the energies attributable to α-hydrogen bonding are already so small that it may be experimentally very difficult to test the reality of α-carbon bonding.

α-Hydrogen bonding is approximately representable by the use of valence bond resonance struc-

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[14] Ref. 15, p. 518.

[15] M. Simonetta and S. Winstein, THIS JOURNAL, **76**, 18 (1954).

[16] R. S. Mulliken, *J. Phys. Chem.*, **56**, 295 (1952).

[17] R. S. Mulliken, C. A. Rieke, D. Orloff and H. Orloff, *J. Chem. Phys.*, **17**, 1248 (1949).

[18] This agreement arises from a cancellation of errors in the assumptions made above. The introduction of the angular distortion in S_{15} reduces it by about a factor of two but the C–H σ-bond is stronger than the C–C π-bond by about that same factor to start with.

tures. The structures that must be considered for the ethylonium ion are shown in Fig. 1.

Results

Reaction Rates and Equilibria.—Taft and Kreevoy[3b,3d] have recently correlated reactivity with structure in a number of reaction series by means of the equations

$$(\Delta F_0 - \Delta F_0{}^0) = (\Sigma\sigma^*)\rho^* + (\Delta n)h \qquad (7a)$$

$$(\Delta H_0 - \Delta H_0{}^0) = (\Sigma\sigma^*)\rho^* + (\Delta n)h \qquad (7b)$$

$$\log (k/k_0) = (\Sigma\sigma^*)\rho^* + (\Delta n)h \qquad (7c)$$

(These correlations were limited to saturated substituents.) The notation in eq. 6 is that of Kreevoy and Taft.[3d]

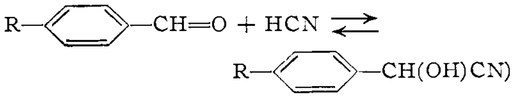
α-Hydrogen bonding provides a straightforward explanation for such an effect and a useful method for estimating its magnitude. For equilibria, equations such as 5 are solved for the general product, the general starting material, the standard product and the standard starting material. The effect of α-hydrogen bonding (for saturated substituents) is given by ΣE (general product) $-$ ΣE (general reactant) $-$ ΣE (standard product) $+$ ΣE (standard reactant). For reaction rates the method is the same, except that a structure must be assumed for the transition state.

In this way calculations have been made of the effect of α-hydrogen bonding on the potential energy of the reactions

$$R_1R_2C{=}O + H_2 \rightleftarrows R_1R_2CH(OH) \qquad (8)$$

$$R_1CH{=}CHR_2 + H_2 \rightleftarrows R_1CH_2CH_2R_2 \qquad (9)$$

$$R_1C{\equiv}CR_2 + 2H_2 \rightleftarrows R_1CH_2CH_2R_2 \qquad (10)$$



(11)

$$R{-}C{\equiv}CH \rightleftarrows R{-}C{\equiv}C^- + H \qquad (12)$$

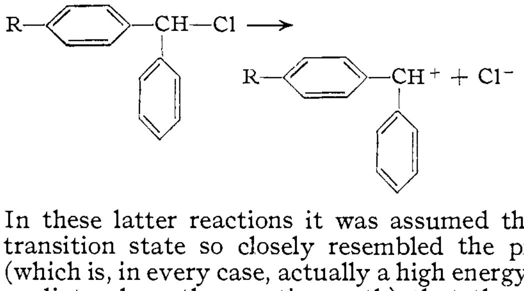
$$RH \rightleftarrows R\cdot + H\cdot \qquad (13)$$

$$R\cdot \rightleftarrows R^+ + e^- \qquad (14)$$

and on the potential energy of activation for the reactions

$$R_1R_2C(OR)_2 + H^+ \longrightarrow R_1R_2COR^+ + HOR \qquad (15)$$

$$R_1R_2R_3CCl \longrightarrow R_1R_2R_3C^+ + Cl^- \qquad (16)$$



(17)

In these latter reactions it was assumed that the transition state so closely resembled the product (which is, in every case, actually a high energy intermediate along the reaction path) that they could be assumed to be the same. This is not a necessary assumption, but, in the absence of more definite information about the transition state, it seems reasonable, and, as will be seen, it leads to good results. In general, the nature of the assumption to be made about the transition state will vary from reaction to reaction. In the first approximation (neglecting the angle of rotation) these calculations indicate that, in each case, the effect of α-hydrogen bonding is almost exactly proportional to the change in the number of α-hydrogen atoms. For example, the calculated effect per hydrogen atom on the activation energy for acetal and ketal hydrolysis (reaction 14) varies smoothly from 0.055β for $\Delta n = 1$ to 0.058β for $\Delta n = 6$. In the next approximation the first figure would be somewhat lower because of the necessary compromises in the angle of rotation, but this lowering is not readily calculated nor is the experimental work sufficiently unambiguous to investigate it.

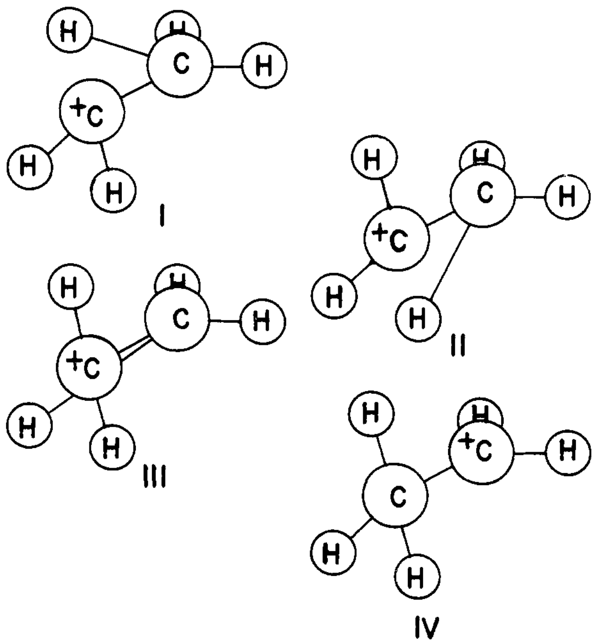


Fig. 1.—The principal resonance structure (IV) and resonance structures showing α-hydrogen bonding (I–III) for the ethylonium ion.

If it is assumed that the Baker–Nathan effect is due to α-hydrogen bonding, the h of eq. 7 can be identified with the effect, per hydrogen, of α-hydrogen bonding, on the energy of reaction or of activation. This is an approximation, of course, since the measured quantities are heats or free energies rather than energies, but it seems reasonable. Table I shows the values obtained for the reactions shown in eq. 8–17 and wherever possible compares them with the empirically obtained values. To convert the theoretical values to usable units, β has been assigned the value 14 kcal./mole, which is the value required to predict the effects of conjugation on many of these same reactions[19] and slightly lower than the value obtained from the resonance energy of benzene.[20,21]

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[19] M. M. Kreevoy and R. W. Taft, Jr., THIS JOURNAL, **79**, 4016 (1957).

[20] C. A. Coulson, "Valence," Oxford at the Clarendon Press, 1952, p. 240.

[21] The lower value of β was obtained from examples with imperfect geometry and probably roughly compensates for the imperfect geometry of the cases discussed here.

TABLE I

EMPIRICAL AND CALCULATED "*h*" VALUES

Reaction	Calcd. "*h*" kcal./mole	Empirical "*h*" kcal./mole
8	0.43	0.56[a]
9	.43	.45[a]
10	.85	.59[a]
11	.03	.04[b,c,f] .06[b,c,g]
12	.00	
13	.79	
14	.00	
15	.80	.76[d]
16	.79	
17	.06	.15[c,e,h] .13[c,e,i] .04[c,e,j]

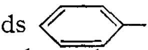
[a] Ref. 3b. [b] J. W. Baker and M. L. Hemming, *J. Chem. Soc.*, 191 (1942). [c] Obtained by assuming that the Hammett σ is the same for all *p*-alkyl groups. [d] Ref. 3d. [e] E. D. Hughes, C. K. Ingold and N. A. Taher, *J. Chem. Soc.*, 950 (1940). [f] At 20°. [g] At 35°. [h] In aqueous acetone at 0°. [i] In aqueous acetone at 25°. [j] In alcohol at 25°.

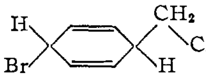
In the calculations involving carbonyl groups the Coulomb integral of the oxygen atom, $\int \psi_O H \psi_O d\tau$, was given a value $^1/_2\ \beta$ higher than that for a carbon atom, and the resonance integral for the carbon–oxygen π-bond, $\int \psi_O H \psi_C d\tau$, was given the value β. These values are satisfactory for calculating resonance energies due to conjugation[19] and the present results are not sharply dependent on the exact values chosen.

In all of these cases α-hydrogen bonding not involving π-orbitals has been neglected, not because it is thought to be vanishingly small, but because it is thought to be nearly the same in starting materials and products. It will therefore, in general, not greatly influence rates or positions of equilibrium, and will have to be sought in subtler ways.

Considering the crudeness of the calculations and the uncertainties in the empirical values, the agreement in Table I is very satisfactory. Together with the fact that the Baker–Nathan effect seems to show a linear dependence on the number of α-hydrogen atoms[3b,3d] the agreement in Table I strongly suggests that α-hydrogen bonding makes up a very substantial part of the Baker–Nathan effect.

Reactions 13 and 14 deserve some further comment. In 13 the predicted Baker–Nathan effect accounts for about half of the observed changes in dissociation energy on going through the series R = CH_3, C_2H_5, *i*-C_3H_7, *t*-C_4H_9,[22] and the rest is due presumably to inductive effects. A more sophisticated calculation using a method such as that proposed by Pariser and Parr[23] would undoubtedly predict a significant Baker–Nathan effect on reaction 14, perhaps even as large as that for reaction 13, but the present theory can in no way predict a Baker–Nathan effect anywhere near as large as the observed effect of structure on reactivity.[24] It seems likely then that the effect of structure on the energy of reaction 14, is governed principally by inductive effects, as was postulated by Smith and Eyring.[25]

β-Hydrogen Bonding.—A "Baker–Nathan order" has been observed for the rates of bromination of compounds —CH_2R,[26] where R was varied from methyl to *t*-butyl. While the experimental evidence is still too sparse to permit definitive conclusions such an effect might very well be due to the contribution of forms such as



to the transition state. Such an effect might be called β-hydrogen bonding, and might well be of the same order of magnitude as α-hydrogen bonding.

Other Effects.—The predicted effects of α-hydrogen bonding on ultraviolet spectra, ionization potentials, bond lengths, bond angles, dipole moments, infrared spectra and deuterium isotope effects on reaction rates are all very similar to the effects predicted by hyperconjugation, and it is not possible to separate them at present. Indeed, it is hard to distinguish either of them from inductive effects. It is therefore only possible to say that no data from these fields are inconsistent with the postulate of important α-hydrogen bonding effects.

Discussion and Conclusions.—α-Hydrogen bonding is closely related to neighboring group participation, which has been described by Winstein and coworkers.[15] The latter effect, however, is larger, occurs only in situations which favor a skeletal rearrangement, and is almost always accompanied by such rearrangement, while α-hydrogen bonding is almost universal, gives rise to smaller effects and alters molecular geometries only in their finer details.

As the theory has been developed here α-hydrogen bonding is related to that portion of hydrogen bonding which is due to electron delocalization, but not to the larger fraction which seems to be due to simple electrostatic interactions.

It is clear that the heart of the present work lies in the assignment of $\int \psi_1 H \psi_3\ d\tau$, the resonance integral for the hydrogen 1s orbital with a p orbital of an atom once removed, equal to $^1/_4\ \beta$. Although the orientation of the hydrogen atom is not perfect for bonding, it is obvious that some bonding is possible, *i.e.*, the integral is not identically zero. Thus the assignment is not unreasonable at worst, and the semi-quantitative agreement in Table I is strong evidence that it is approximately correct.

Quantitative predictions of the present paper suffer, of course, not only from the imperfections of the model, but also from the general crudeness of the empirical L.C.A.O.—M.O. method of calculation. The inadequacies of this method have been discussed elsewhere.[6,23] The present theory is cap-

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[22] J. S. Roberts and H. A. Skinner, *Trans. Faraday Soc.*, **45**, 339 (1949).

[23] R. Pariser and R. C. Parr, *J. Chem. Phys.*, **21**, 466 (1953).

[24] (a) D. P. Stevenson, *Disc. Faraday Soc.*, **10**, 35 (1951); (b) M. Szwarc, *ibid.*, **10**, 336 (1951).

[25] R. P. Smith and H. Eyring, THIS JOURNAL, **75**, 5183 (1953).

[26] (a) E. Berliner and F. Berliner, *ibid.*, **71**, 1195 (1949); (b) **72**, 222 (1950).

able of being developed in a more rigorous fashion as hyperconjugation has been developed,[3e,27] but even the crude calculations seem to give an adequate measure of the Baker–Nathan effect, and they have the advantage that the method is very easily applicable to a wide variety of systems.

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(27) (a) C. A. Coulson and V. A. Crawford, *J. Chem. Soc.*, 2052 (1953); (b) Y. I'Haya, *J. Chem. Phys.*, **23**, 1165 (1955); (c) Y. I'Haya, *ibid.*, **23**, 1171 (1955).

[CONTRIBUTION FROM THE RESEARCH AND DEVELOPMENT DEPARTMENT OF THE ATLANTIC REFINING COMPANY]

Irradiation of Petroleum Hydrocarbons. I. Electron Bombardment of Liquid Butanes[1]

BY V. J. KEENAN, R. M. LINCOLN, R. L. ROGERS AND H. BURWASSER

RECEIVED OCTOBER 24, 1956

The irradiation of liquid *n*-butane by 1 million volt electrons yields principally mixtures of octenes and octanes. Smaller amounts of hydrogen, ethane, butene and higher products, *i.e.*, C_{12}, C_{16} and C_{20} hydrocarbons are also encountered. Isobutane yields, in addition to such products, methane, propylene and large amounts of C_7 hydrocarbons which are attributed to the formation of C_3 fragments and their subsequent participation in addition or combination reactions. The carbon skeletons and relative amounts of the C_8 isomers have been determined but do not unequivocally indicate the manner of formation of these compounds.

Introduction

Prediction of the effect of atomic radiation upon complex hydrocarbons and their mixtures requires elucidation of mechanisms for simple hydrocarbon systems. Steacie[2] has recently reviewed the literature of free radical mechanisms. In addition, several reviews on the effect of radiation upon organic compounds have appeared.[3-5] To gain further information on the chemical nature of the liquid products we have undertaken the study of the irradiation of simple hydrocarbons. Such information is fundamental to the industrial application of atomic radiation to organic chemical reactions.

For the irradiation experiments here reported, the butanes were chosen as the simplest hydrocarbons which can demonstrate the role of primary, secondary and tertiary carbon atoms in the reaction mechanism. A one-million volt electron accelerator was chosen for its high and alterable energy as well as its experimental convenience.

Experimental

The equipment consisted of two parts: the electron accelerator and an enclosed system for circulating liquid butane and exposing it to the electron beam. The accelerator was a General Electric Company Resonant Transformer,[6] operating at 1 mev. and 0.2 to 1.0 ma. beam out.

The chemical reaction system comprised a reaction cell equipped with a circulating pump, Dry Ice condensers and cooling coil, and reservoirs for the removal of samples and addition of reactants. Initial irradiations of *n*-butane were carried out using a conventional centrifugal pump which required correction of experimentally determined values to compensate for leakage. Later irradiations of *n*-butane and the first irradiations of isobutane were performed using various capacity diaphragm pumps. These were troublesome because of "vapor lock" and their low rate of flow (up to 0.2 liter per min.) which to avoid overheating the butane, limited the maximum current of the electron beam to 0.4 ma. Finally, a Chempump model E proved satisfactory for leak-proofness and capacity.

The condensers, reservoir, thermocouple well and sampling pot were all of Pyrex, fitted together by ground glass joints. The tubing and coil were of copper, the pump of stainless steel, and the valves, tubing fittings and irradiation cell were of brass. Metal to glass connections were made by means of ground semi-ball joints.

The irradiation cell (Fig. 1) was a shallow brass cylinder with an internal diameter of 3 in. and an internal height of $^5/_{16}$ in. which when filled with liquid hydrocarbon was sufficient to absorb virtually all of the electrons entering the system. The maze absorbed only 15% of the radiation while providing more uniform irradiation of the flowing liquid sample. The cell outlet was located at the upper edge to permit gases to escape while maintaining the cell filled with liquid. A 2 mil stainless steel disc provided a cover for the cell through which 90% of the electron energy passed. The base of the cell contained an integral cooling chamber through which a Dry Ice–alcohol solution was circulated. A clamping ring and through-bolts held the assembly together.

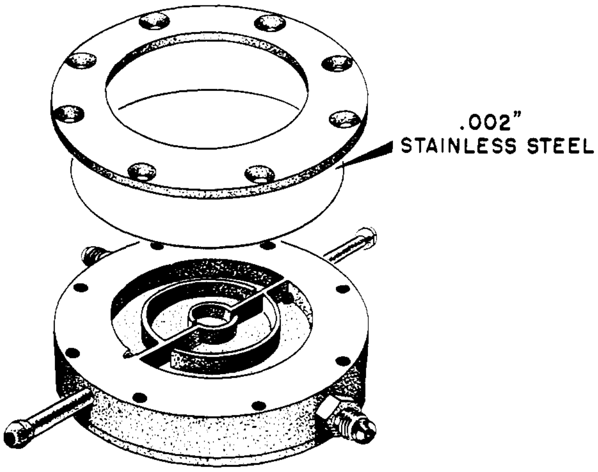

Fig. 1.—Irradiation cell.

The reaction system, including the irradiation cell and the Chempump had a capacity of about 1200 ml. of liquid. Residence times, under the electron beam, could be varied between 5 and 50 seconds per pass when using the Chempump. Reaction temperatures were maintained at −30 to −50° by circulating the butanes through the Dry Ice-cooled coil in series with the reaction cell. A thermocouple was located in the effluent from the cell to measure the temperature. Gases formed during the irradiation were led through a Dry Ice condenser and thence through a sampling manifold to a gas meter.

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(1) Presented at the 130th Meeting of the American Chemical Society, Atlantic City, N. J., September, 1956.

(2) E. W. R. Steacie, "Atomic and Free Radical Reactions," Reinhold Publ. Corp., New York, N. Y., 1954.

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