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separated into volatile and nonvolatile fractions as described above. Again, ethyl acetate was identified by gas chromatographic analysis as a minor component (0.0071 mol) of the distillate, but no diethyl ether was detected.

The nonvolatile residue (0.5 g) was recrystallized from hot water to give an additional 0.3 g of **6** (mp 216–217 °C). The mother liquor was evaporated to dryness, and the IR spectrum of the residue indicated that this was a mixture of **6** and *o*-acetamidobenzoic acid (**8**).

Registry No. 1, 525-76-8; **2a**, 67-56-1; **2b**, 64-17-5; **2d**, 141-43-5; **3** (R = Me), 82666-35-1; **5**, 4005-06-5; **6**, 58426-37-2; **7**, 118-92-3; **8**, 89-52-1; **9**, 82666-36-2; 2-acetamidoethanol, 142-26-7; *N*-(2-hydroxyethyl)-2-methylquinazol-4-one, 10376-59-7; *o*-acetamido-*N*-(2-hydroxyethyl)benzamide, 63703-31-1; 2-[[(1,1-dimethoxy)ethyl]amino]benzoic acid, 82666-37-3.

Radical Reorganization and Bond Energies in Organic Molecules

R. T. Sanderson[†]

Arizona State University, Tempe, Arizona 85281

Received August 11, 1981

The results of a study of contributing bond energies and bond dissociation energies of organic molecules are given. A set of theoretical and empirical contributing bond energies is presented that are accurately additive to give atomization energies and heats of formation of organic compounds of most common functional types. With the help of these values and literature values for radicals, the reorganizational energies of 27 common radicals have been determined and are reported herein. Breaking a bond requires both supplying the contributing bond energy and reorganizing the radicals formed. The bond dissociation energy is the sum of the contributing bond energy and the reorganizational energies of the radicals. These radical energies include the following hydrocarbon series (kcal/mol): benzyl, −13.9; allyl, −10.5; *tert*-butyl, −1.7; isopropyl, 0.7; *n*-propyl, 1.3; ethyl, 1.5; methyl, 3.6; vinyl, 10.0; and phenyl, 12.3. Also reported are the following (kcal/mol): phenoxy, −24.0; nitro, −10.5; acetyl, −7.1; benzoyl, −7.1; aldehyde, −5.8; methyl sulfone, −5.1; methoxy, −4.0; phenylthio, −3.9; ethoxy, −3.8; carboxylic acid, −3.5; acetate, −2.9; hydroxymethyl, −1.7; thiol, 2.9; methylthio, 5.1; hydroxyl, 9.7; methylamino, 12.1; amino, 19.5; cyano, 24.8.

The strength of a chemical bond, as evaluated by the bond dissociation energy (BDE), has two components. One is the contributing bond energy (CBE), which is that part of the total atomization energy of the molecule that a particular bond contributes. Contributing bond energies, impossible to evaluate experimentally except for diatomic molecules wherein they are identical with BDE, or as average bond energies in molecules where all bonds are alike, can be calculated accurately by the theory of polar covalence.[1] They are assumed to be accurate when the sum for all the bonds in the molecule equals the experimental atomization energy. The experimental atomization energy is the difference between the sum of the energies required to atomize each of the elements involved, and the standard heat of formation of the compound, in the gaseous state. The second component of the BDE is the reorganizational energies of the radicals formed by the breaking of the bond. If the radicals are single atoms, no further change occurs, the reorganizational energies being zero. If the radical consists of more than one atom, however, the liberated bonding electron will influence the remaining bonds in the radical. If possible, it will strengthen the bonding, releasing energy that reduces that needed for bond dissocn. If it cannot strengthen the bonding, it will weaken it, absorbing energy and thus increasing the energy required for dissociation. The purpose of this paper is to show how both components may be evaluated and, to a useful degree, understood.

Table I. Reorganizational Energies of Some Free Radicals

radical	H_f°	ref	E_R, kcal/mol
C_6H_5O	11.4	6	−24.0 (−24.0)
$C_6H_5CH_2$	45.1	6	−13.9 (−13.9)
$CH_2{=}CHCH_2$	41.4	6	−10.5 (−10.1)
NO_2	6.0	6	−10.5 (−10.5)
CH_3CO	−5.8	6	−7.1 (−7.1)
C_6H_5CO	26.1	6	−7.1 (−6.5)
CHO	7.7	6	−5.8 (−5.8)
CH_3SO_2	−57.2	6	−5.1 (−5.9)
CH_3O	3.8	6	−4.0 (−4.0)
C_6H_5S	56.8	6	−3.9 (−3.7)
C_2H_5O	−4.1	6	−3.8 (−3.7)
COOH	−53.3	6	−3.5 (−3.3)
CH_3COO	−49.6	6	−2.9 (−2.2)
t-C_4H_9	10.5	7, 8	−1.7 (−2.0)
CH_2OH	−6.2	6	−1.7 (−1.9)
i-C_3H_7	20.6	7	0.7 (0.7)
n-C_3H_7	22.6	6, 9	1.3 (1.2)
C_2H_5	28.2[a]	7[a]	1.5 (1.9)
SH	33.1	6	2.9 (3.3)
CH_3	35.1	10, 11	3.9 (3.6)
CH_3S	34.2	6	5.1 (5.8)
OH	9.2	6	9.7 (9.7)
$CH_2{=}CH$	68	6	10.0 (10.0)
CH_3NH	45.4	6	12.1 (11.7)
C_6H_5	77.7	6	12.3 (12.2)
NH_2	47.2	6	19.5 (18.0)
CN	101	6	24.8 (24.8)

[a] References 6 and 9 give 25.9 corresponding to E_R = −0.7.

Special emphasis is placed on the evaluation of the reorganizational energies of free radicals, for these can be more informative than either the standard heat of formation of the radical or the bond dissociation energy, from the viewpoint of understanding the origins of bond strength and the mechanisms of chemical reactions involving free radicals. Textbooks of organic chemistry commonly include a table of dissociation energies of specific bonds in familiar compounds, which could advanta-

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[†] Address correspondence to 4725 Player Drive, Fort Collins, CO 80525.

(1) R. T. Sanderson, "Chemical Bonds and Bond Energy", 2nd ed., Academic Press, New York, 1976.

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geously be replaced by a table of radical reorganizational energies (see Table I), since these apply to all combinations of any given radical. For example, all bonds to phenyl are about 12 kcal/mol more difficult to break than would be expected from the CBE, because the bond cannot be broken without simultaneously weakening the residual bonding in the phenyl radical. Part or all of this extra energy, however, may come from a favorable reorganization of the other radical. For example, breaking a phenyl group from diphenylmethane would be about 2 kcal easier than expected from the CBE because the large (14 kcal/mol) reorganizational energy of the benzyl radical more than compensates for the requirement of the phenyl radical.

The evaluation of the CBE's is based on a simple theory of polar covalence, as detailed in my book on chemical bonds.[1] A brief review of this theory will serve to prepare for the evaluation and discussion of reorganizational energies of free radicals. Any polar covalent bond in a gaseous molecule may be viewed usefully as a blend of two hypothetical extremes, a nonpolar covalent form involving even sharing of the bonding electrons, and an ionic form involving the monopolization of the bonding electrons by one of the atoms. The bond energy, E_c, of the nonpolar form is simply the geometric mean of the two homonuclear single covalent bond energies, corrected for any difference between the observed bond length, R_o, and the sum of the two nonpolar covalent radii, R_c: $E_c = R_c(E_{AA}E_{BB})^{1/2}R_o$. The bond energy of the ionic form, E_i, is simply the factor 33 200 times the product of unit opposite charges, divided by the bond length: $E_i = 33\,200/R_o$, where the energy is in kilocalories/mole and the bond length in picometers. The actual bond is pictured as a blend of these two contributions: $E = t_cB_c + t_iE_i$, where t_c and t_i are the blending coefficients, the sum of which is 1.00. For multiple bonds, E is multiplied by a factor of 1.52 for all double bonds and 1.84 for carbon–carbon triple bonds. For aromatic rings the factor is $1 + 0.33n$ where n is the average number of π electrons/bond.

The blending coefficients are easily evaluated, t_i being half the difference between the partial charges on the two bonded atoms. The partial charges in turn are easily determined as the ratio of the change in electronegativity undergone by the atom in joining the compound to the change that would correspond to the acquisition of unit charge. The latter change is simply a constant, 2.08, times the square root of the atomic electronegativity. The electronegativity in the compound is determined as the geometric mean of all the atomic electronegativities before combination. This is based on the principle of electronegativity equalization,[2] according to which, when atoms join together in compounds, they become adjusted to the same intermediate electronegativity in the compound. Recent quantum mechanical studies[3,4] support this principle. Application of this theory will be clarified by an example presently. The theory has proven successful in the calculation of energies of thousands of bonds in more than a thousand molecules, both organic and inorganic.

First, by assuming bond energies of hydrogen to primary and secondary carbon to be essentially the same, and C′C′, C′C″, and C″C″ bonds also to be essentially equal, it was possible to equate the experimental atomization energies of the normal alkanes through decane with the number of each kind of bond, and by solving simultaneous equations derive CBE's of 82.78 kcal/mol for C–C and 98.81 kcal/mol for C–H. These values applied to ethane, in which all bonds involve primary carbon, give an atomization energy of 675.6 kcal/mol compared with the experimental value of 675.4, justifying the above assumption.

Next, this result was examined by use of the theory of polar covalence. Let us consider a methylene group as adequately representative of normal alkanes. Its electronegativity is the geometric mean of 2.79 for C and 3.55 for each of two atoms of 1 H, or 3.63. The carbon, being initially more electronegative than the hydrogen, has acquired more than half share of the bonding electrons. This excess of electrons increases the shielding of the carbon nucleus, while increasing the interelectronic repulsions, allowing the cloud to expand and diminishing the effective nuclear charge. Reduced effective nuclear charge acting over increased distance corresponds to diminished electronegativity, from 3.79 to 3.63, or by 0.16. Complete acquisition of an electron would have decreased the electronegativity by 4.05, so the partial charge on carbon is $-0.16/4.05 = -0.04$. On the other hand, removal of part of the electron from hydrogen results in diminishing the shielding of the hydrogen nucleus and allowing the residual cloud to be drawn closer to the nucleus. This increased effective nuclear charge acting over a shorter distance corresponds to an increase in electronegativity, from 3.55 to 3.63, or by 0.08. Complete loss of an electron would correspond to a change of 3.92, so the partial charge on hydrogen is $0.08/3.92 = 0.02$. The ionic blending coefficient is half the difference between charges: $(0.02 - -0.04)/2 = 0.03$. The covalent blending coefficient is $1.00 - 0.03 = 0.97$.

The polarity is too slight to have an appreciable effect on the bond length, so the experimental bond length is the same as the nonpolar covalent radius sum, 77 pm for carbon plus 32 pm for hydrogen = 109 pm. Uniquely for hydrogen, a correction in the homonuclear bond energy must be made for the partial positive charge. The correction factor is 1.00 minus the partial charge on H, so the corrected homonuclear bond energy is 104.2 × 0.98 = 102.1 kcal/mol. The geometric mean with carbon is 92.5 kcal. The separate covalent and ionic contributions may now be calculated:

$$t_cE_c = (0.97 \times 92.5 \times 109)/109 = 89.7 \text{ kcal/mol}$$

$$t_iE_i = (0.03 \times 33\,200)/109 = 9.1 \text{ kcal/mol}$$

Their sum, 98.8 kcal/mol, is exactly the C-H bond energy obtained empirically.

Note that the slight polarity of the bond, only 0.03, nevertheless accounts for more than 9% of the total energy. Polarity always increases the bond strength. In any polar covalent bond, a part of the total possible covalent energy is replaced by an ionic contribution, and the ionic contribution is always larger than that part of the total covalent energy which it replaces. Here 2.8 kcal of covalent energy is replaced by 9.1 kcal of ionic energy, strengthening the bond by 6.3 kcal. (The theory is equally successful in calculating the energies of more polar bonds. For example, for gaseous KCl the covalent contribution is calculated to be 7.25 and the ionic contribution 94.75 kcal/mol, the sum of which is 102.0 kcal/mol. The experimental value is 101.7 kcal.)

Application of the simple theory to organic compounds of all common functional types has been reasonably successful.[1] However, improved accuracy depends on taking into account relatively minor but nevertheless significant complications, resulting from carbon–carbon bond strengthening by chain branching and bond weakening by steric repulsions between nearby branches. Numerous

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(2) R. T. Sanderson, *Science*, 114, 670 (1951).

(3) R. G. Parr, R. A. Donnelly, M. Levy, and W. E. Palke, *J. Chem. Phys.*, 68, 3801 (1978).

(4) P. Politzer and H. Weinstein, *J. Chem. Phys.*, 71, 4218 (1979).

Table II. Empirical Contributing Single Bond Energies

	$C'(H_3)$	$C''(H_2)$	$C'''(H)$	C''''	vinyl	phenyl
H	98.8	98.8	98.8	98.8	98.8	97.8
C'	82.8	82.8	83.5	84.1	84.4	84.4
C''	82.8	82.8	83.1	83.4	84.4	84.4
C'''	83.5	83.1	82.5	80.7		
C''''	84.2	83.4	80.7	78.3		
C- to:						
CHO	84.4	84.4				87.1
CO	84.5	84.8	84.5	82.9	(87.5)	87.5
COOH	84.4	84.4				85.1
$CONH_2$	83.4	83.4				
COF	85.0					
COCl	84.5					86.5
COBr	85.4					85.7
COI	84.7					86.4
CN	86.4	90.0	(90)			(90)
NH_2	64.7	65.8	67.6	69.3		72.7
NHR	68.6	70.8	(73)	(74)		73.7
NR_2	70.8	72.0				(75)
NO_2	65.6	67.5	69.8	(73)		68.0
OH	78.9	81.7	85.0	86.8		88.0
OR	83.0	86.3	88.2	89.1		89.7
OOC	82.0	86.3	88.2	89.1	89.7	89.7
ONO_2	83.8	86.6				
SH	67.3	67.3	68.2	(69)		69.1
SR	69.0	69.2	70.3	71.0		71.2
SOR	66.5	68.6			69.8	70.0
SO_2R	69.5	71.2	72.8			(73.4)
F[a]	106.0	107.6	108.3	113.1	109.0	111.8
Cl[a]	80.9	81.6	83.7	85.6	80.6	82.1
Br[a]	66.9	68.4	69.9	70.8	66.0	67.0
I[a]	53.4	53.9	55.5	55.3		51.9

[a] Values applicable to only one halogen per carbon.

Table III. Group and Bond Contributing Energies Calculated from Theory of Polar Covalence

group or bond	CBE, kcal/mol	group or bond	CBE, kcal/mol
CHO	269.5	i-C_3H_7	858.6
CO	176.3	n-C_4H_9	1137.6
COO	284.6	t-C_4H_9	1141.8
COOH	392.5	CH_2=CH	440.9
$CONH_2$	452.9	CH_2=$CHCH_2$	722.9
COF	302.4	C_6H_5	1222.8
COCl	265.1	$C_6H_5CH_2$	1504.8
COBr	249.0	C_6 (benzene)	733.8
COI	233.0	C=C	144.5
CN	208.1	C≡C	195.6
NH_2	188.0	CC=	84.4
NH	94.0	=CC=	86.7
OH	112.2	CC≡	87.3
ONO_2	268.3	=CC≡	89.2
NO_2	215.6	≡CC≡	92.4
SH	88.5	aromatic rings	
SO	91.7	C-C	122.3
SO_2	198.3	C-N	109.9
CH_3	296.4	C-S	82.3
C_2H_5	576.8	C-C_6H_5	84.4
n-C_3H_7	857.2	C_6H_5-C_6H_5	87.5

elaborate schemes have been proposed in the past[5] to account for these factors. For this work, relatively simple empirical corrections were obtained from a study of atomization energies of all the alkane isomers through C_9 and were found satisfactorily applicable to both branched hydrocarbons and their derivatives.

An earlier attempt[1] to evaluate reorganizational energies was based on neglect of these factors and on somewhat uncertain BDE values. This paper reports greatly improved values based on more accurate CBE's and BDE's. Reorganizational energies of 27 free radicals are presented in Table I. These depend for accuracy on reliable heats of formation of radicals, not always certain. Therefore, heats of formation from which reorganizational energies were in part derived are included in the table with references to the source.

There are two principal ways of calculating bond dissociation energies. One is to subtract the standard heat of formation of a compound from the sum of the standard heats of formation of the two radicals:

$$\mathrm{BDE} = \Delta H_f^\circ(\mathrm{I}) + \Delta \mathrm{Hf}^\circ(\mathrm{II}) - \Delta H_f^\circ(\mathrm{I{-}II}) \qquad (1)$$

The other is to add the reorganizational energies, E_R, of the radicals I and II to the contributing bond energy:

$$\mathrm{BDE} = \mathrm{CBE} + E_R(\mathrm{I}) + E_R(\mathrm{II}) \qquad (2)$$

These two equations were used in evaluating the reorganizational energies, in the following way. Bond dissociation energies were calculated by eq 1, using the heats of formation tabulated by Kerr and Trotman-Dickenson,[6] or more recent data,[7] and the heats of formation of gaseous molecules recommended by Cox and Pilcher.[5] CBE's were obtained from Tables II and III and used in eq 2 to determine the reorganizational energies. First, compounds of hydrocarbon radicals with hydrogen and halogens were used to evaluate the reorganizational energies of these radicals, since the E_R values for H, F, Cl, Br, and I are of course zero. Reorganizational energies of the hydrocarbon radicals were then used to determine by difference the values for other radicals. Heats of formation of compounds not found in the literature were calculated from the atomization energies of the elements and from the data of Tables II and III. In a few instances where eq 1 and 2 failed to give bond dissociation energies agreeing within about 1 kcal/mol, the standard heat of formation of the compound was calculated, and, if significantly different, used in place of the literature value. The average difference in BDE as calculated by the two equations was less than 0.4 kcal/mol for the 270 bonds studied, well within the probable limits of experimental error.

Reorganizational energies can also be evaluated as the difference between the atomization energy of the radical and the sum of the contributing bond energies of the same bonds within the molecule. Such values are presented in parentheses in Table I. They are considered generally less reliable since they depend heavily on the accuracy of the individual experimental heats of formation and there is no possibility of averaging several similar values, as was done for the preferred reorganizational energies.

The determination of reorganizational energies and their use in evaluating bond dissociation energies is illustrated by some representative examples in Table IV.

Many schemes for empirical evaluation of bond energies and heats of formation of organic compounds have of course been proposed.[5] The data of Tables II and III have the advantage of simplicity without sacrificing accuracy.

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(5) J. D. Cox and G. Pilcher, "Thermochemistry of Organic and Organometallic Compounds", Academic Press, New York, 1970.

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(7) G. M. Atri, R. R. Baldwin, G. A. Evans, and R. W. Walker, *J. Chem. Soc.*, J. C. S. *Faraday Trans. 2*, **74**, 366 (1978).

(8) C. E. Canosa and R. M. Marshall, *Int. J. Chem. Kinet.*, **13**, 303 (1981).

(9) T. N. Bell, K. A. Perkins, and P. G. Perkins, *J. Phys. Chem.*, **83**, 2321 (1979).

(10) B. A. Robaugh and G. D. Stein, *Int. J. Chem. Kinet.*, **13**, 445 (1981).

(11) S. W. Benson, P. A. Knoot, and S. P. Heneghan, *Int. J. Chem. Kinet.*, **13**, 518 (1981).

Table IV. Representative Calculations of Some Bond Dissociation Energies

bond I	bond II	$\Delta H_f°$(compd)/ CBE	$\Delta H_f°$(I)/ E_R(I)	$\Delta H_f°$(II)/ E_R(II)	BDE/ BDE
$C_6H_5CH_2$	CN	47.9	45.1	101	98.2
		87.3	−13.9	24.8	98.2
C_6H_5	OH	−23.0	77.7	9.2	109.9
		88.0	12.3	9.7	110.0
$C_6H_5CH_2$	$CH_2CH{=}CH_2$	27.7	45.1	41.4	58.8
		82.8	−13.9	−10.5	58.4
CH_3SO_2	t-C_4H_9	−113.1	−57.2	10.5	66.4
		73.0	−5.1	−1.7	66.2
n-C_3H_7	NO_2	−29.9	22.6	6.0	58.5
		67.5	1.3	−10.5	58.3
C_2H_5	NH_2	−11.4	28.2	47.2	86.8
		65.8	1.5	19.5	86.8
CH_3	COOH	−103.3	35.1	−53.3	85.1
		84.4	3.6	−3.5	84.5
CH_3COO	$CH{=}CH_2$	−78.3	−49.6	68	96.7
		89.7	−2.9	10.0	96.8

Table V. Representative Atomization Energies and Heats of Formation (Experimental and Calculated from Tables II and III; Kilocalories/Mole)

		atomization energy		heat of formation	
compd	formula	calcd	exptl	calcd	exptl
n-propyl fluoride	C_3H_7F	964.8	964.7	−67.3	−67.2
2,2′-difluorobiphenyl	$C_{12}H_8F_2$	2561.1	2558.2	−50.9	−48.0
2-chloro-2-methylbutane	$C_5H_{11}Cl$	1505.2	1507.1	−46.5	−48.4
chlorobenzene	C_6H_5Cl	1304.9	1305.2	12.5	12.2
1-bromohexane	$C_6H_{13}Br$	1766.8	1767.7	−35.0	−35.9
benzyl bromide	C_7H_7Br	1573.2	1573.6	16.5	16.9
allyl iodide	C_3H_5I	776.8	777.0	23.1	22.9
benzoyl bromide	C_7H_5OBr	1557.5	1557.5	−11.6	−11.6
sec-butyl alcohol	$C_4H_{10}O$	1335.9	1335.8	−69.9	−70.0
2,5-dimethylphenol	$C_8H_{10}O$	1989.0	1989.9	−38.0	−38.9
methyl *tert*-butyl ether	$C_5H_{12}O$	1610.3	1610.4	−67.7	−67.6
propanal	C_3H_6O	930.7	931.6	−44.6	−45.5
ethyl phenyl ketone	$C_9H_{10}O$	2148.2	2148.3	−25.9	−26.0
adipic acid	$C_6H_{10}O_4$	1992.6	1994.0	−205.4	−206.8
isopropyl 3-pentenoate	$C_6H_{14}O_2$	2321.4	2320.6	−102.4	−101.6
cyclohexanethiol	$C_6H_{12}S$	1740.3	1742.0	−19.8	−22.8
methyl phenyl sulfide	C_7H_8S	1659.4	1658.9	23.1	23.6
ethyl allyl sulfoxide	$C_5H_{10}OS$	1528.6	1528.4	−24.9	−24.7
methyl phenyl sulfone	$C_7H_8O_2S$	1860.4	1861.4	−59.5	−60.5
diphenylamine	$C_{12}H_{11}N$	2687.0	2687.5	54.7	54.2
p-nitroaniline	$C_6H_6O_2N_2$	1669.3	1669.4	16.3	16.2
3,5-dimethylpyridine	C_7H_9N	1764.0	1763.6	17.0	17.4
acrylonitrile	C_3H_3N	738.2	739.1	45.0	44.1
hexanamide	$C_6H_{13}ON$	1954.3	1956.5	−76.6	−78.8

The data of Table III are obtained directly from the simple theory of polar covalence[1] and, therefore, provide a basis for a fundamental understanding of the bond strength on the properties of atoms. The data of Table II are roughly in agreement with the theoretical energies also but in addition take into account in an empirical manner the minor factors mentioned earlier. The average difference between calculated and experimental atomization energies for all the compounds studied—nearly 800 organic molecules—is less than 1 kcal/mol, generally well within the possible limits of experimental error. Since the average molecule studied contains about 18 bonds (molecules containing as many as 60 bonds are included in the study) and has an average atomization energy of about 1800 kcal/mol, the agreement is within 0.06%. A sampling of the results is provided in Table V.

Of special interest in Table II is evidence suggesting a possible weakening effect of hydrogen attached to a polyvalent atom on its other bonds. Note the bond energies of C, CH, CH_2, and CH_3 to CH_3, COO, NH_2, NH, N, O, OH, NO_2, S, SH, SO_2, F, Cl, Br, and I, all of which decrease from quaternary to primary carbon. Notice also that bonds to N are stronger than to NH, which in turn are stronger than to NH_2, and that bonds to S are stronger than to SH, and bonds to OR stronger than to OH. Further study of this apparent phenomenon should be rewarding.

It would be desirable, of course, to provide theoretical explanations for all reorganizational energies. This can easily be done for radicals that can rearrange to form stable molecules, such as CO, COO, OO, NO_2, SO_2, or alkane diradicals that can form C=C bonds. The reorganizational energy is simply the difference between the bonding energy of the molecule and the energy of the same bonds in the original compound. It is, of course, negative, making the bond dissociation that liberates such radicals that much easier. For example, the splitting of a methyl radical from an acetate radical is exothermic because of the high stability of the released carbon dioxide.

For radicals that cannot form stable molecules by reorganization, explanation of the energy is likely to be more qualitative at best and, in most instances, highly speculative, or lacking. The high values (Table I) for phenoxy and benzyl radicals seem to reflect the tendency of the oxygen or methylene group to become involved with the π electrons of the ring. In general, breaking one of two bonds to oxygen appears to strengthen the remaining bond somewhat, although the opposite is true in the dissociation of water. There is need for enlightenment as to why, for example, a released bonding electron should weaken the bonds in a phenyl radical or strengthen the bonds in a *tert*-butyl radical.

Fortunately, it is not necessary to understand fully the origin of all reorganizational energies in order to recognize their role in bond dissociation and to make practical use of them. In particular, the series of values for hydrocarbon radicals can be especially helpful in explaining various aspects of hydrocarbon chemistry.

Registry No. Benzyl, 2154-56-5; allyl, 1981-80-2; *tert*-butyl, 1605-73-8; isopropyl, 2025-55-0; *n*-propyl, 2143-61-5; ethyl, 2025-56-1; methyl, 2229-07-4; vinyl, 2669-89-8; phenyl, 2396-01-2; phenoxy, 2122-46-5; nitro, 10102-44-0; acetyl, 3170-69-2; benzoyl, 2652-65-5; aldehyde, 2597-44-6; methyl sulfone, 4853-80-9; methoxy, 2143-68-2; phenylthio, 4985-62-0; ethoxy, 2154-50-9; carboxylic acid, 2564-86-5; acetate, 13799-69-4; hydroxymethyl, 2597-43-5; thiol, 13940-21-1; methylthio, 7175-75-9; hydroxyl, 3352-57-6; methylamino, 15622-51-2; amino, 13770-40-6; cyano, 2074-87-5; *n*-propyl fluoride, 460-13-9; 2,2′-difluorobiphenyl, 388-82-9; 2-chloro-2-methylbutane, 594-36-5; chlorobenzene, 108-90-7; 1-bromohexane, 111-25-1; benzyl bromide, 100-39-0; allyl iodide, 556-56-9; benzoyl bromide, 618-32-6; *sec*-butyl alcohol, 78-92-2; 2,5-dimethylphenol, 95-87-4; methyl *tert*-butyl ether, 1634-04-4; propanal, 123-38-6; ethyl phenyl ketone, 93-55-0; adipic acid, 124-04-9; isopropyl 3-pentenoate, 62030-41-5; cyclohexanethiol, 1569-69-3; methyl phenyl sulfide, 100-68-5; ethyl allyl sulfoxide, 34757-40-9; methyl phenyl sulfone, 3112-85-4; diphenylamine, 122-39-4; *p*-nitroaniline, 100-01-6; 3,5-dimethylpyridine, 591-22-0; acrylonitrile, 107-13-1; hexanamide, 628-02-4.

Thermolysis of Trialkylnitrosoureas: Formation of an Unusual Product

Sandra S. Singer

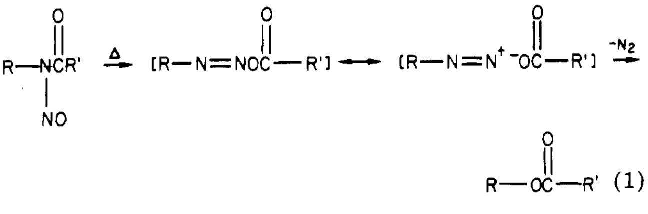
Chemical Carcinogenesis Program, NCI-Frederick Cancer Research Facility, Frederick, Maryland 21701

Received January 13, 1982

The thermolysis of four trialkylnitrosoureas, 1,1,3-trimethyl-1-nitrosourea (**1**), 3,3-diethyl-1-methyl-1-nitrosourea (**2**), 1-ethyl-3,3-dimethyl-1-nitrosourea (**3**), and 1,3,3-triethyl-1-nitrosourea (**4**), was carried out neat, in protic and aprotic solvents. When the thermolysis was run neat or in aprotic solvents, **4** gave as much as 70% of *N,N*-diethylalanine ethyl ester (**9**). Ethyl *N,N*-diethylcarbamate (**8**) (about 10%) was the only other product isolated. In protic solvent, however, **8** was the principal product. Neat thermolysis of **2** and **3** gave products analogous to those obtained from **4** but in much lower yields. Thermolysis of **1** did not give any product comparable to **9**. Tetramethylurea was a major product from the thermolyses of **1** and **3**. Decomposition of **3** was faster than any of the other three compounds studied, but **3** did not give high yields of products. Addition of CuCl to the reaction mixture caused the reaction products to change dramatically. The appropriate dialkylnitrosamine and the denitrosated urea were then the major products.

Introduction

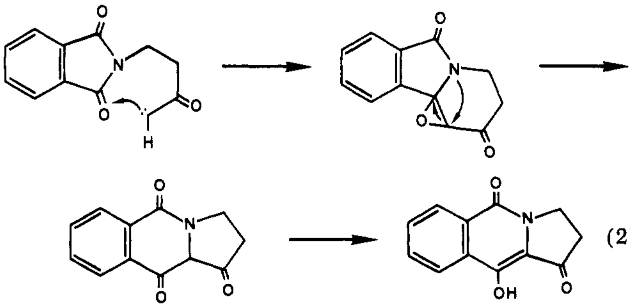
The thermolysis of nitrosamides was studied carefully by White,[1] Streitweiser,[2] Huisgen,[3] and others[4] about 25 years ago. At that time, it was established that the major pathway for thermolysis of nitrosamides,[1] nitrosocarbamates,[5] and nitroamides[6] was via rearrangement to a diazo compound that subsequently lost N_2 (N_2O in the case of nitroamides) to give an ester (eq 1). This reaction was shown to occur by way of a tight ion pair that had a lifetime sufficient for partial scrambling of O^{18} from specifically labeled carbonyl.[1]



$$\mathrm{R{-}\underset{\underset{NO}{|}}{N}\overset{\overset{O}{\|}}{C}R'} \xrightarrow{\Delta} [\mathrm{R{-}N{=}NO\overset{\overset{O}{\|}}{C}{-}R'}] \longrightarrow [\mathrm{R{-}N{=}N^{+}\,{}^{-}O\overset{\overset{O}{\|}}{C}{-}R'}] \xrightarrow{-N_2} \mathrm{R{-}O\overset{\overset{O}{\|}}{C}{-}R'} \quad (1)$$

At higher temperatures, free-radical processes competed with the diazo ester rearrangement, and olefinic products were observed when R contained a β-hydrogen.[3]

While the thermolyses of nitrosamides and nitrosocarbamates have been studied in some detail, nitrosoureas have received only minimal attention. Werner in 1919 demonstrated the thermal decomposition of methylnitrosourea to give nitrogen, methyl isocyanate, and water.[8] Boivin and Boivin later studied the decomposition of methylnitrosourea in boiling water and the products derived from the reaction of isocyanate produced with alkylamine.[9] However, neat thermolyses or thermolyses of substituted nitrosoureas in aprotic solvents do not appear to have been studied in any detail. The thermolysis reactions of four trialkylnitrosoureas produce carbamates, as expected, but the nitrosoureas also undergo an unusual insertion reaction that appears to be the result of a carbene insertion into an amide C–N bond. This is not a common reaction of carbene or carbenoid species, although a similar insertion was observed by Krauser and Watterson.[7] The carbene derived from 1-diazo-4-phthalimido-2-butanone gave 1,5,8-trioxobenz[*f*]indolizidine as the final product of a rearrangement that was initiated by insertion of the carbene across the imide carbonyl (eq 2).



(2)

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