The Correlation of Secondary α-Deuterium Isotope Effects with Primary Nitrogen Isotope Effects in the Thermolysis of Azo Compounds[1]

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Abstract: Nitrogen-15 isotope effects are reported for three aralkyl azo compounds that undergo thermal decomposition by three different mechanisms. The nitrogen effects, combined with the previously reported carbon-13 and secondary α-deuterium effects, are used to calculate the force field changes that take place for each reactant molecule on conversion to its activated complex. For bonds that are only slightly weakened (or tightened) in the transition state, self-consistent force fields are formed when the relative reduction (or increase) in the stretching and bending reactant force constants are the same.

The secondary α-deuterium kinetic isotope effect has been shown to be a very sensitive tool to probe the bonding changes that a molecule undergoes in its conversion from the reactant state to the transition state.[2] In a reaction proceeding by a unimolecular decomposition mechanism such as $R_1R_2CHX \rightarrow [R_1R_2CH\cdots X]^{\ddagger} \rightarrow R_1R_2CH + X$, the decrease in the bending force constant associated with the H–C–X group, accompanied by the stretching of the C–X bond, has been shown to be responsible for the generation of a secondary α-deuterium kinetic isotope effect.[2e,g] If the C–X bond is almost completely ruptured in the transition state, as in a limiting SN1 solvolysis, the central carbon atom has been suggested to resemble an sp^2-hybridized olefinic or aldehydic carbon atom.[2b] Thus, in the transition state, the H–C–X bending force constant might approach the value for the C–H out-of-plane bending force constant for an aldehydic or olefinic C–H bond. The isotope effect, observed in a limiting reaction such as this, yields information only about the difference in the nature of bonding between two extreme states, *viz.*, the reactant where a full bond exists between carbon and X, and the transition state where, in this hypothetical example, there is virtually no bond between carbon and X. Very little information is available for transition states positioned between these two extreme models. If there were less than complete rupture, the magnitude of the α effect is expected to be smaller than that observed in limiting cases. Just how much smaller the effect will be is not known because *it is not known how the H–C–X bending force constant varies with changes in the C–X stretching force constant.*

Some unimolecular decompositions, however, are accompanied by α effects smaller than those observed in limiting cases of decomposition. The smaller than normal effects have been attributed to only partial C–X bond rupture at the transition state.[2d,3] Similarly, small inverse isotope effects, observed in the Diels–Alder reaction and in the addition of radicals to olefins, can be explained if only partial bond formation is required at the transition state.

The independent determination of the relative changes in the C–X bond strength in going from reactant to transition state, obtained from the study of isotopic substitution at X, combined with the measured α effects in the same system might enable the determination of the dependence of the change in the H–C–X bending force constant on the change in the C–X stretching force constant. We describe here the experimental determinations and the corresponding "exact" calculations of kinetic isotope effects for three such systems as discussed above.

Experimental Section

Azobis-α-phenylethane[2c,4] (mp 72.2–73.0°), α-phenylethylazo-2-propane[2d,5] (n^{25}D 1.4910), and α-phenylethylazomethane[2f] (n^{25}D 1.5072) were prepared by methods described previously. Ethylbenzene (Eastman) was dried and distilled from sodium through a 12-in. Heli Pak column, n^{25}D 1.4930 (lit.[6] n^{25}D 1.4933). Diphenyl ether (Matheson Coleman and Bell) after initial drying was also distilled through a 12-in. Heli Pak column. Benzoquinone (Eastman) was purified by steam distillation and sublimation.

Thermal decomposition of azobis-α-phenylethane was allowed to proceed in ethylbenzene while the solvent system for α-phenylethylazo-2-propane and α-phenylethylazomethane was 0.13 *M* benzoquinone in diphenyl ether solution. In all cases the solutions were approximately 0.02 *M* in azo compound. The thermal decomposition reactions were carried out in sealed tubes fitted with breakseal and standard taper joint. Those carried to complete decomposition were contained in tubes of about 14-cc volume containing about 5 ml of solution while solutions for partial decomposition runs were contained in tubes of approximately 75-cc volume containing 50 ml of azo compound solution. Prior to the sealing of each tube, the contents were thoroughly degassed on a high-vacuum line by several cooling–pumping–warming cycles. When no further gas evolved, as evidenced by a steady reading on a Pirani gauge, the tube was sealed by allowing the heated glass to collapse. The tubes were immersed in a large oil bath maintained at a constant temperature to within ±0.05°. After the allotted reaction

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[2] (a) E. A. Halevi, *Progr. Phys. Org. Chem.*, **1**, 109 (1963); (b) A Streitwieser, Jr., R. H. Jagow, R. C. Fahey, and S. Suzuki, *J. Am. Chem. Soc.*, **80**, 2326 (1958); (c) S. Seltzer, *ibid.*, **83**, 2625 (1961); (d) S. Seltzer, *ibid.*, **85**, 14 (1963); (e) A. A. Zavitsas and S. Seltzer, *ibid.*, **86**, 3836 (1964); (f) S. Seltzer and F. T. Dunne, *ibid.*, **87**, 2628 (1965); (g) M. Wolfsberg and M. Stern, *Pure Appl. Chem.*, **8**, 225 (1964); **8**, 325 (1964); (h) T. W. Koenig and W. D. Brewer, *Tetrahedron Letters*, 2773 (1965); *cf.* M. J. Goldstein, *ibid.*, 1601 (1964); (i) S. Borcic, M. Nikoletic, and D. E. Sunko, *J. Am. Chem. Soc.*, **84**, 1615 (1962).

[3] (a) S. Seltzer, *ibid.*, **87**, 1534 (1965); (b) D. E. Van Sickle, *ibid.*, **86**, 3091 (1964); (c) M. Field, A. P. Stefani, and M. Szwarc, *ibid.*, **84**, 4451 (1962); (d) W. A. Pryor, R. W. Henderson, R. A. Patsiga, and N. Carroll, *ibid.*, **88**, 1199 (1966).

[4] S. G. Cohen and C. H. Wang, *ibid.*, **77**, 2457 (1955).

[5] C. G. Overberger and A. V. Di Giulio, *ibid.*, **80**, 6562 (1958).

[6] J. A. Riddick and E. E. Toops, Jr., "Techniques of Organic Chemistry," Vol. VII, A. Weissberger, Ed., Interscience Publishers, Inc., New York, N. Y., 1955, p 77.

time, the tubes were removed, cooled, and stored in the freezer at −20°.

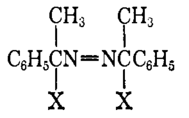
Before opening, each tube was cooled, in a Dry Ice–chloroform–carbon tetrachloride mixture and connected through a stopcock and a liquid-nitrogen-cooled radiator trap to a Toepler pump. The noncondensable gases were pumped in this way from the reaction tube to a calibrated gas buret. To ensure complete recovery of nitrogen, the contents of the reaction tube were subjected to at least ten warming–cooling–pumping cycles. Finally the quantity of gas was measured in order to calculate, *f*, the fraction of reaction.

Mass spectral analysis was achieved on a Consolidated-Nier isotope ratio instrument, Model 21-201, by standard techniques. The determination of the 29/28 mass ratio of each sample was bracketed by the determination of this ratio in a standard sample of prepurified nitrogen gas. All determinations were normalized to a common value for this standard sample. Corrections were made for imperfect collector resolution (−0.000121). After these corrections were made, the experimental kinetic isotope effects were calculated in the standard way.[7]

Purification of nitrogen was accomplished by heating the gas mixture over freshly oxidized copper wire at 800° for approximately 18 hr. The contents were then passed through a radiator trap cooled in liquid nitrogen to remove water and carbon dioxide.

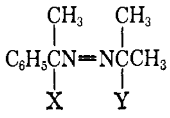
Results

The nitrogen isotope effects, k_{14}/k_{15}, were determined for the thermal decomposition of azobis-α-phenylethane (1), α-phenylethylazo-2-propane (II), and α-phenylethylazomethane (III). Thermal decompositions of I were carried out in ethylbenzene at 105° while the decompositions of II and III were allowed to proceed in a diphenyl ether solution containing 0.13 *M* benzoquinone at 143 and 161°, respectively. To ensure quantitative recovery of the nitrogen gas, each sample was subjected to more than ten cool–pump–warm cycles. The quantities of nitrogen at complete reaction were somewhat less than the expected amount. For compounds I, II, and III, 94–99, 98.5–99.5, and about 95.5% of the expected gas were recovered, respectively. This might be the result of incomplete removal of the gas and/or a small amount of side reaction. No observable impurities were found in the nitrogen gas obtained from azobis-α-phenylethane, but that obtained from α-phenylethylazo-2-propane and α-phenylethylazomethane was shown to contain small amounts of propane and methane, respectively. The nitrogen from these two sources was purified by oxidizing the small amounts of hydrocarbon with hot copper oxide. The nitrogen was separated from the products of oxidation in the standard way. The mass spectral analyses were accomplished with a Consolidated-Nier Model 21-201 isotope ratio instrument. The results are shown in Table I. The average value of the 29/28 ratio at complete decomposition for each compound was used to calculate k_{14}/k_{15} at each individual fraction of reaction, *f*.[7] The observed average deviation in $[(k_{15}/k_{14}) - 1]$ is about 6% for azobis-α-phenylethane and α-phenylethylazomethane and about 3.5% for α-phenylethylazo-2-propane. Errors in the determination of $[(k'/k) - 1]$ generated by uncertainties in determining *f* and mass ratios have been discussed previously.[8] If we examine our least certain set of data, *i.e.*, for azobis-α-phenylethane, and use the average deviation in the mass ratio at complete reaction as an estimate for the error in the ratio, we calculate that the expected error in $[(k_{15}/k_{14}) - 1]$ is about 4.5% when $f \sim 0.2$ and the error in determining *f* is about 2%.



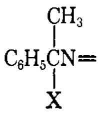
$\mathrm{C_6H_5\underset{X}{\overset{CH_3}{C}}N{=}N\underset{X}{\overset{CH_3}{C}}C_6H_5}$

Ia, X = H
b, X = D



$\mathrm{C_6H_5\underset{X}{\overset{CH_3}{C}}N{=}N\underset{Y}{\overset{CH_3}{C}}CH_3}$

IIa, X = Y = H
b, X = D; Y = H
c, X = H; Y = D



$\mathrm{C_6H_5\underset{X}{\overset{CH_3}{C}}N{=}NCY_3}$

IIIa, X = Y = H
b, X = D; Y = H
c, X = H; Y = D

Table I. Kinetic Nitrogen Isotope Effects

f[a]	m/e (29/28)[b]	k_{14}/k_{15}
	Azobis-α-phenylethane[d]	
0.0982	0.007141	1.022_1
0.1522	0.007127	1.025_0
0.1771	0.007152	1.021_5
1.00[c]	0.007266	
1.00[c]	0.007313	
1.00[c]	0.007294	
		Av $1.022_9 \pm 0.001_4$
	α-Phenylethylazo-2-propane[e]	
0.0790	0.007281	1.016_0
0.2020	0.007291	1.015_7
0.0667	0.007289	1.014_7
0.1360	0.007296	1.014_3
1.00[c]	0.007386	
1.00[c]	0.007394	
1.00[c]	0.007400	
		Av $1.015_2 \pm 0.000_5$
	α-Phenylethylazomethane[f]	
0.0795	0.007216	1.014_7
0.1381	0.007230	1.013_1
0.1484	0.007237	1.012_1
0.2098	0.007236	1.012_8
1.00[c]	0.007319	
1.00[c]	0.007317	
1.00[c]	0.007319	
1.00[c]	0.007316	
		Av $1.013_2 \pm 0.000_8$

[a] Fraction of reaction. [b] Mass ratio corrected for improper resolution. [c] Ten half-lives of reaction. [d] In ethylbenzene at 105.02 ± 0.05°. [e] In benzoquinone (0.13 *M*)–diphenyl ether solution at 143.20 ± 0.05°. [f] In benzoquinone (0.13 *M*)–diphenyl ether solution at 161.00 ± 0.05°.

Discussion

Table II. Summary of Secondary α-Deuterium Isotope Effects in the Thermal Decomposition of Azo Compounds

Compd	Temp, °C	k_H/k_D	Ref
Ia/Ib	105.28	1.27 ± 0.03	2c
IIa/IIb	143.20	$1.14_8 \pm 0.01_2$	2d
IIa/IIc	143.20	$1.03_6 \pm 0.00_7$	2d
IIIa/IIIb	161.00	1.13 ± 0.01	2f
IIIa/IIIc	161.00	0.97 ± 0.01	2f

We have previously reported secondary α-deuterium isotope effects in the thermal decomposition of azobis-α-phenylethane (I), α-phenylethylazo-2-propane (II), and α-phenylethylazomethane (III).[2c,d,f] The results are summarized in Table II. In addition, the C^{13}-isotope effect in the azomethyl group on decomposition of IIIa was reported to be 1.0068 ± 0.0006. In harmony with these results is the suggestion that I thermally decomposes with simultaneous equal homolytic rupture of both carbon–nitrogen bonds to yield nitrogen and two α-phenylethyl radicals.[2c] α-Phenylethyl-

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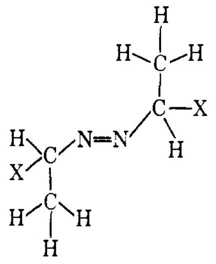
(7) J. Bigeleisen and M. Wolfsberg, *Advan. Chem. Phys.*, **1**, 30 (1958).

(8) J. Bigeleisen and T. L. Allen, *J. Chem. Phys.*, **19**, 760 (1951).

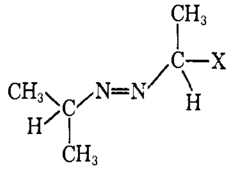
azomethane (III), however, decomposes in two discrete steps. Because the methyl radical is less stable than the α-phenylethyl radical by about 25 kcal/mole,[9] the predominant mode of decomposition is rupture of the benzylic carbon–nitrogen bond of III, followed by the scission of the methyl carbon–nitrogen bond in a second step. The inverse α-deuterium isotope effect for the decomposition of IIIa *vs.* IIIc together with the very small C^{13} isotope effect in the azomethyl group of III suggests that the azomethyl carbon–nitrogen bond tightens a small amount during the stretching of the benzylic carbon–nitrogen bond. II decomposes by a mechanism intermediate between that for I and III. Both carbon–nitrogen bonds of II rupture simultaneously but to unequal degrees. Rationalization for this behavior can be found again in the relative stabilities of the incipient carbon radicals. The 2-propyl radical is less stable than the α-phenylethyl radical but more stable than the methyl radical.[9] Within this group of three related compounds the mechanism of decomposition varies widely enough to permit a correlation between the changes in the H–C–N bending and C–N stretching force constants.

Wolfsberg and Stern[2g] have made "exact" calculations of isotope effects on model systems. Based on a program of Schachtschneider[10] which is used to calculate vibrational frequencies from a complete set of force constants, atomic masses, and geometry of the molecule, Wolfsberg's program calculates isotope effects between two states from the frequencies generated by the Schachtschneider program. Calculation of kinetic isotope effects requires then a knowledge of force constants and geometry of the reactant and transition states. Force constants for the transition state are unknown; however, those constants which involve atoms far removed from the site of reaction are generally assumed not to change in going from reactant to transition state. Those closer to the reaction site can be evaluated, though generally not independently, by altering reactant state force constants in such a way as to fit the experimentally observed isotope effects.[11] Important mechanistic information can be obtained from the magnitude and direction of the force constant changes in going from reactant to transition states.

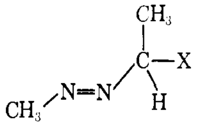
Geometries of Reactant and Transition States. The models adopted here for the fitting of calculated with observed isotope effects is similar to that used previously for the calculation of the ratio of imaginary frequencies encountered in the decomposition of azobis-α-phenylethane and azobis-α-phenylethane-β,β,β-d_3.[11b] The 16-atom pseudo-molecule IV, where the masses of the X atoms were set equal to 77.0, was used to calculate nitrogen-15 and α-deuterium isotope effects in the decomposition of I. Bond lengths and angles were suggested from data on analogous compounds.[12] Carbon–hydrogen and carbon–carbon distances were set equal to 1.10 and 1.54 A, respectively, except for the C–X distance which was assumed to be 1.52 A. Carbon–nitrogen and nitrogen–nitrogen bond lengths were made to equal 1.47 and 1.24 A, respectively. Tetrahedral angles were adopted for the methyl groups but the X–C–C angles were increased to 112° while the benzylic H–C–C angles were reduced to 106° to account for the larger volume of phenyl compared to hydrogen. Finally the N=N—C angles were set equal to 120°. The geometry of I in the transition state was considered to be the same as adopted for I in the reactant state except for a few changes. The carbon–nitrogen bond length was increased to 1.71 A while the nitrogen–nitrogen distance was reduced to 1.17 A. As the incipient benzylic radicals move away from nitrogen, it is expected that the three atoms attached to the benzylic carbon would tend to become coplanar with the central carbon atom and so the X–C–C and the X–C–H angles were set equal to 111°. Furthermore the X–C–N and C–N–N angles were allowed to become 101 and 105°, respectively. The 19-atom pseudo-molecule V and the 13-atom pseudo-molecule VI, where phenyl groups of mass 77.0 are represented by X atoms, were chosen as models for reactants II and III, respectively. In each of these, the geometry of the azo-α-phenylethyl portions of the molecule were identical with that same part found in IV. The remaining groups, *i.e.*, the isopropyl in V and the methyl in VI, *trans* to the α-phenylethyl group, were assumed to have tetrahedral angles and standard bond lengths. To obtain models for the transition state, changes were made in the geometry of V and VI in a way to be consistent with the detailed mechanism for decomposition of II and III that has been suggested previously. As in the reactant, the coordinates of the atoms contained in the benzylic nitrogen portions of the transition states corresponding to V and VI were identical with that same part of the molecule for the transition state corresponding to IV. The nitrogen–nitrogen bond distances in the transition states of V and VI, however, were not reduced as much as in the transition state model of IV. While the N–N bond length of IV was reduced to a value midway between that for the nitrogen molecule (1.098 A) and the reactant (1.24 A), the transition state N–N bond lengths of V and VI were assumed to be more reactant like. Reduction in N–N bond lengths corresponding to only 31 and 25% of the total difference between N–N bond lengths in the reactant and the nitrogen molecule were made for V and VI, respectively. The methyl-



IV



V



VI

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[9] C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p 50.

[10] J. H. Schachtschneider and R. G. Snyder, *Spectrochim. Acta*, **19**, 117 (1963).

[11] (a) M. J. Goldstein and G. L. Thayer, Jr., *J. Am. Chem. Soc.*, **87**, 1933 (1965); (b) S. Seltzer and E. J. Hamilton, Jr., *ibid.*, **88**, 3775 (1966).

[12] L. E. Sutton, Ed., "Tables of Interatomic Distances and Configuration in Molecules and Ions," Special Publication No. 18, The Chemical Society, London, 1965.

nitrogen bond length in VI was unchanged while the isopropyl–nitrogen bond length was increased only about 5%. In any case, however, it has been shown that isotope effects calculated from different geometrical arrays of atoms, but from similar force constant changes, are similar.[2g] The conclusions would not be expected to differ significantly from a choice of different geometrical models.

Force Fields. A. Azobis-α-phenylethane. The force fields chosen for each of the three reactants were essentially very similar and obtained from reported force constants for analogous groupings of atoms when available. The valence force constants used for the reactants are shown in Table III. Unfortunately, constants involving vibrational modes of carbon–nitrogen and nitrogen–nitrogen bonds are not as well known. All of the constants involving nitrogen atoms are assumed values but derived by comparison with known values of multiple bonded carbon–carbon and carbon–nitrogen bonds (see footnote in Table III).

Table III. Valence Force Constants in the Azo Reactant Molecules[a]

		Ref
Methyl CH stretch	4.716	*b*
Methinyl CH stretch	4.623	*b*
Alkyl-alkyl CC stretch	4.394	*b*
Aryl-alkyl CC stretch	4.84	*c*
CN stretch	5.0	*d*
-N=N- stretch	10.0	*e*
Methyl HCH bend	0.543	*b*
Methyl HCC bend	0.650	*b*
Methinyl HCC bend	0.667	*b*
Aryl-alkyl CCC bend	1.084	*b*
C—C—N bend	1.1	*f*
C—N=N bend	1.2	*g*
Torsion about single bond	0.01	*b*
Torsion about N=N	0.70	*h*

[a] Stretching force constants are in mdynes/A. Bending force constants are in mdynes A/(rad)². [b] J. H. Schachtschneider and R. G. Snyder, *Spectrochim. Acta*, **19**, 117 (1963). [c] Average of C—C and C—C≡ stretching force constants in G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., New York, N. Y., 1945, p 193. [d] Force constants recorded for C—C, C≡C, and C≡N stretches are 4.50, 15.6, and 17.73 mdynes/A, respectively (Herzberg, footnote *c*). This would suggest that a reasonable value for the C–N stretching constant would be 5.1 mdynes/A. A rounded value of 5.0 was chosen because of the uncertainty. [e] Assumed to be similar to the C=C stretching force constant, 9.6 mdynes/A (Herzberg, footnote *c*). [f] Assumed to be similar to C—C—C bending constant; see footnote *b*. [g] Assumed to be similar to C—C=C bending constant (E. B. Wilson, Jr., and A. J. Wells, *J. Chem. Phys.*, **9**, 319 (1941)). [h] See Wilson and Wells, footnote *g*.

The force fields of the transition state were constructed in such a way as to be consistent with the detailed thermal decomposition mechanisms originally suggested by the secondary α-deuterium isotope effects. The symmetric stretch of both carbon–nitrogen bonds was chosen as the reaction coordinate for the decomposition of azobis-α-phenylethane. This was accomplished by introducing a negative interaction stretching force constant, f_{ij}, which obeys eq 1; the stretching force constants for each carbon–nitrogen bond, f_{ii} and f_{jj}, were chosen to be positive

$$f_{ii}f_{jj} - f_{ij}^2 \leqslant 0 \qquad (1)$$

and equal. The interaction force constant was generally chosen so that the left side of eq 1 was generally very small and negative (∼ −0.001). In this way an almost flat energy barrier is produced.

With these restrictions in mind it remains to find a consistent set of force constants for the transition state that by calculation will reproduce the observed isotope effects within experimental uncertainty. Forty-six coordinates were used to fully described the stretching, bending, and torsional vibrations of model IV for azobis-α-phenylethane. Of these, all but 11 involve vibrational modes that might be expected to change very little or not at all in going from reactant to transition state. The force constants for these 35 "inert" coordinates were therefore assumed to be the same in both reactant and transition state. The 11 "active" coordinates include the nitrogen–nitrogen and carbon–nitrogen stretching and four pairs of bending modes.[13] Three of the bending modes refer to the angles made by nitrogen, the benzylic carbon atom, and the three atoms bonded to that carbon atom. The fourth arises from the angle made by the N=N—C atoms. The results of calculations with two different sets of force constant changes are given in Table IV.[14] It was assumed here that the ratio (∼0.4) of α-H—C—N bending force constants between transition and reactant states, needed to reproduce the secondary deuterium effect, would be the same for the remaining "active" bending constants.

Table IV. Isotope Effects Calculated from Reactant and Transition State Force Constants for Azobis-α-phenylethane[a]

	Reactant	Transition state IVa	 IVb
C—N stretch	5.0	2.5	0.1
N=N stretch	10.0	12.5	12.5
H—C—N bend	0.60	0.230	0.230
X—C—N bend	1.10	0.450	0.450
C—C—N bend	1.10	0.450	0.450
C—N=N bend	1.20	0.450	0.450
f_{ij}		−2.5001	−0.10001
Isotope effects	Obsd[b]	Calcd[b]	
$k_{\alpha\text{-H}_2}/k_{-\alpha D_2}$	1.27 ± 0.02	1.269	1.270
k_{14}/k_{15}	1.0229 ± 0.0014	1.0136	1.0230

[a] Stretching force constants are in mdynes/A. Bending force constants are in mdynes A/(rad)². [b] At 378°K.

There is a greater margin for adjustment of the stretching force constants. Reduction in carbon–nitrogen force constants can be balanced in part by an increase in the nitrogen–nitrogen stretching constant. The maximum increase (∼25%) in the nitrogen–nitrogen constant, consistent with almost complete rupture of the C–N bonds and calculated nitrogen isotope effect, was adopted, however, to take account of the diminution in activation energy that might result from increased overlap of the incipient free electrons at each end of the azo linkage with the nitrogen p orbitals in the transition state.

B. α-Phenylethylazomethane. In addition to the deuterium and nitrogen isotope effects, information is

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(13) The paired coordinates arise from the point symmetry that the molecule possesses.

(14) In these and subsequent calculations only the force fields that we have used that can reasonably reproduce the measured isotope effects are shown in Tables IV, V, and VI.

available on the effect of C^{13} substitution in the azomethyl group. The very small carbon effect suggests, at the outset, a slightly tighter methyl–nitrogen bond in the transition state compared to the reactant and places further restraint on the choice of transition-state force constants. As in the previous example, calculations were performed by assuming that the symmetrical stretching mode of both carbon–nitrogen bonds is converted to the reaction coordinate. In Table V, a set of internally consistent transition state force constants is shown which can be used to successfully reproduce the observed isotope effects within experimental uncertainty. It should be pointed out that the increase (15%) in the methyl–nitrogen *stretching* force constant from reactant to transition state is the same as the increase in the H—C—N (methyl) and C—N=N (methyl) *bending* force constants.[15] The ratio of transition state to reactant α-H—C—N (benzylic) bending force constant was adjusted to 0.27 in order to reproduce the observed α-deuterium isotope effect at that position. The other bending force constants at that carbon, *viz.*, the X—C—N, C—C—N, and the C—N=N (benzylic), were also adjusted to this same ratio. Finally, if it is assumed that almost complete rupture of the benzylic C—N bond has been attained in the transition state and that this C—N stretching constant falls to 0.1, there is no other choice but to increase the N=N stretching constant from 10.0 to 12.0 in order to reproduce the nitrogen isotope effect.

Table V. Isotope Effects Calculated from Reactant and Transition-State Force Constants for α-Phenylethylazomethane[a]

	Reactant	Transition state VIA	VIB	VIC
C—N (benzylic) stretch	5.0	0.1	0.1	0.0
C—N (methyl) stretch	5.0	5.65	5.0	5.0
N=N stretch	10.0	12.0	13.5	13.5
H—C—N (benzylic) bend	0.60	0.162	0.162	0.162
H—C—N (methyl) bend[b]	0.60	0.69	0.68	0.68
C—C—N bend	1.10	0.297	0.297	0.297
X—C—N bend	1.10	0.297	0.297	0.297
C—N=N (benzylic) bend	1.20	0.324	0.324	0.324
C—N=N (methyl) bend	1.20	1.38	1.36	1.36
f_{ij}		−0.75167	+0.75167	0.0

Isotope effects	Obsd[c]	Calcd[c]		
$k_{\alpha\text{-H}}/k_{\alpha\text{-D}}$ (benzylic)	1.13 ± 0.01	1.120	1.122	1.120
$k_{\alpha\text{-H}_3}/k_{\alpha\text{-D}_3}$ (methyl)	0.97 ± 0.01	0.966	0.960	0.968
k_{12}/k_{13}	1.0068 ± 0.0006	1.0061	1.0030	1.0063
k_{14}/k_{15} (benzylic)		1.0260	1.0268	1.0248
k_{14}/k_{15} (methyl)		1.0000	1.0008	1.0000
k_{14}/k_{15} (av)	1.0132 ± 0.0008	1.0130	1.0138	1.0124

[a] Stretching force constants are in mdynes/A. Bending force constants are in mdynes A/(rad)^2. [b] All three H-C-N bending modes were assigned the same force constant. [c] At 434°K.

Two other models were tested to see if they might also plausibly describe the changes accompanying formation of the transition state. The first (VIB) uses the asymmetric stretching motion of the two carbon–nitrogen bonds as the decomposition mode. This is accomplished by using the same force constants as in VIA (Table V) except that the sign of the interaction stretching force constant, f_{ij}, is now positive. By slight adjustment of force constants, all but the C^{13}-isotope effect is reproduced fairly well. To bring the carbon effect in line would require a further reduction in the methyl C—N stretching force constant accompanied by an increase in the benzylic C—N or N=N stretching constants. This would appear to be an improbable model since both a reduction in the methyl C—N stretching constant from reactant to transition state and an increase in the methyl H—C—N bending constant are required to reproduce the C^{13} and the methyl-d_3 isotope effects.

The second alternative (VIC) allows the two C—N stretching motions to become independent of each other. This is accomplished by removing the interaction force constant and setting the transition state benzylic C—N stretching force constant to zero. If the remaining "active" force constants are allowed to have values similar to those for model VIB, all measured isotope effects can be reproduced by calculation. Here too, as in VIB, the difficulty of reconciling an increase in the methyl H—C—N bending force constants with no change in the methyl C—N stretching force constant still exists. It would appear that VIA is the most reasonable model. In any case all the models are consistent with extensive rupture of the benzylic carbon–nitrogen bond together with less change in the strength of the methyl carbon–nitrogen bond.

C. α-Phenylethylazo-2-propane. The information gained from the calculations on azobis-α-phenylethane and α-phenylethylazomethane was used here to reach a consistent solution for the transition state force field of α-phenylethylazo-2-propane. This is shown in Table VI. Since f_{ij} is negative and conforms to eq 1, the mode of decomposition is a symmetric stretch of both carbon–nitrogen bonds. In the transition state, the benzylic carbon–nitrogen bond, however, is considerably weaker than the carbon–nitrogen bond on the other side of the azo linkage.

Table VI. Isotope Effects Calculated from Reactant and Transition State Force Constants for α-Phenylethylazo-2-propane[a]

	Reactant	Transition state V
C—N (benzylic) stretch	5.0	0.1
C—N (2-propyl) stretch	5.0	4.0
N=N stretch	10.0	12.0
H—C—N (benzylic) bend	0.60	0.126
H—C—N (2-propyl) bend	0.60	0.480
C—C—N (benzylic) bend	1.10	0.232
C—C—N (2-propyl) bend	1.10	0.880
X—C—N bend	1.10	0.232
C—N=N (benzylic) bend	1.20	0.252
C—N=N (2-propyl) bend	1.20	0.960
f_{ij}		−0.63246

Isotope effects	Obsd[b]	Calcd[b]
$k_{\alpha\text{-H}}/k_{\alpha\text{-D}}$ (benzylic)	1.15 ± 0.01	1.1493
$k_{\alpha\text{-H}}/k_{\alpha\text{-D}}$ (2-propyl)	1.036 ± 0.007	1.0400
k_{14}/k_{15} (benzylic)		1.0248
k_{14}/k_{15} (2-propyl)		1.0052
k_{14}/k_{15} (av)	1.0152 ± 0.0005	1.0150

[a] Stretching force constants are in mdynes/A. Bending force constants are in mdynes A/(rad)^2. [b] At 416°K.

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(15) Changes in the α-H–C stretching force constants have been assumed to be negligible here since it has been shown from the temperature dependence of secondary α-deuterium effects[2e] that these involve changes mainly in the bending force constants.[2g]

Starting with the α-deuterium effect in the propyl group, it is found that a reduction of the reactant H–C–H (2-propyl) bending constant by 20% satisfactorily reproduced that isotope effect. The reasonable assumption that the other bending constants, associated with the 2-propyl carbon atom, are also undergoing a reduction of 20% upon conversion to the transition state, is also made. Moreover, this same relative change is incorporated into the 2-propyl carbon–nitrogen stretching constant. If now, it is assumed that almost complete rupture of the benzylic C–N bond ensues, the nitrogen isotope effects can be reproduced by strengthening the nitrogen–nitrogen stretching constant by 20%.

Undoubtedly, other force fields can be used that might lead to almost as good a fit as shown in Table VI, but it would seem that these might not be as internally self-consistent. As a first approximation then it appears from this study that, for small normal or inverse secondary α-deuterium isotope effects, the relative change in the H–C leaving group bending force constant from reactant to transition state, reflects the same change in the C leaving group stretching force constant.

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Organic Photochemistry. XXVII.[1] Electronically Excited State Structures

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Abstract: A series of 4,4-disubstituted cyclohexadienones, differing in the electronegativity of the 4 substituents, was synthesized and the triplet energies were determined. It was found that electronegative substituents served to lower the triplet energy. This was taken to indicate an enhanced β-carbon electron density in the excited triplet relative to the ground state. A small but significant shift of 0–0 emission to higher energy was found on proceeding to glasses of progressively greater polarity and hydrogen bonding ability. The triplet lifetimes at 77°K were similar for 4,4-diphenylcyclohexadienone and 4-methyl-4-trichloromethylcyclohexadienone. The vibrational structure for the series of dienones was of the same type and characteristic of $n-\pi^*$ emission. The triplet emission was found to be parallel to singlet absorption suggesting an $n-\pi^*$ assignment to the triplet. Configuration interaction calculations were carried out including the p_y orbital system for a series of ketones. A good correlation of theory with observation was found for the energies of the $n-\pi^*$ singlets, the $\pi-\pi^*$ singlets, the $n-\pi^*$ triplets, and the $\pi-\pi^*$ triplets. The excited state electron distributions are discussed for the four states of photochemical interest.

One critical point in organic photochemistry is the identification and description of electronically excited species involved in reactions. Once these have been achieved a starting point for correlating electronic configuration with observed photochemical behavior is available. For example, where the triplet state is the reacting species, it would be of considerable help to know the relative energies of the triplet excited states of differing configuration. Thus, although the lowest energy singlet state of dienones and enones is $n-\pi^*$, as evidenced by absorption data,[3] this is not necessarily true for the corresponding triplets.[5]

A second point of interest is the electron distribution and the electronic properties in general of different electronically excited states, $n-\pi^*$ and $\pi-\pi^*$; the triplets are of particular interest. While it is well known that the $\pi-\pi^*$ singlets of conjugated carbonyl compounds are usually more electron rich in the carbonyl group than is the ground state[4] and similarly that the $n-\pi^*$ singlets are less electron rich[6] at oxygen than in the ground state, similar information is not available about the triplet configurations.[7,8] The present study describes some results bearing on these two aspects.

One approach to the problem utilized the four disubstituted dienones: 4,4-dimethylcyclohexadienone (**1**),[9] 4,4-diphenylcyclohexadienone (**2**),[8,10] 4-methyl-4-

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[1] For paper XXVI note H. E. Zimmerman and J. O. Grunewald, *J. Am. Chem. Soc.*, **89**, 3354 (1967).

[2] (a) National Science Foundation Predoctoral Fellow, 1962–1966; (b) Research Associate, University of Wisconsin, 1963–1965; (c) Woodrow Wilson Fellow, 1960–1961; National Institutes of Health Fellow, 1961–1964.

[3] R. S. Mulliken, *J. Chem. Phys.*, **3**, 564 (1935); H. L. McMurry, *ibid.*, **9**, 231, 241 (1941); M. Kasha, *Discussions Faraday Soc.*, **9**, 14 (1950); note also ref 4.

[4] E. M. Kosower and D. C. Remy, *Tetrahedron*, 281 (1959), and related papers for enones.

[5] A triplet of given configuration will in general have a lower energy than the corresponding singlet. This singlet–triplet splitting is small for $n-\pi^*$ states (note J. W. Sidman, *J. Chem. Phys.*, 27, 429 (1957)) compared to $\pi-\pi^*$ splitting and thus for a given molecule with the lowest excited singlet being $n-\pi^*$; it is still possible for the energy decrease on going from the $\pi-\pi^*$ singlet to the $\pi-\pi^*$ triplet to be sufficient to result in the $\pi-\pi^*$ triplet being the lower energy state.

[6] H. McConnell, *J. Chem. Phys.*, 20, 700 (1952).

[7] It was noted[8] that to a first approximation one might anticipate the electron distribution in $n-\pi^*$ singlets and triplets to be similar but that the same could not be assumed true of the $\pi-\pi^*$ configurations.

[8] H. E. Zimmerman and D. I. Schuster, *J. Am. Chem. Soc.*, **84**, 4527 (1962).

[9] F. G. Bordwell and K. M. Wellman, *J. Org. Chem.*, **28**, 1347 (1963).

[10] H. E. Zimmerman and D. I. Schuster, *J. Am. Chem. Soc.*, **83**, 4486 (1961).