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CYCLOPROPYLCARBINYL FREE RADICALS, HEXACYCLOPROPYLETHANE

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Several cases have been reported (1) in which radical-forming reactions are accelerated by the introduction of a cyclopropyl substituent directly on the incipient radical center. It is not clear, however, just how the acceleration is best explained. A concerted multiple bond cleavage reaction leading directly to the allylcarbinyl system might reflect a driving force from relief of strain accompanying the opening of a three-membered ring. Transition state charge polarization (2) in a radical-forming reaction could produce an acceleration reflecting a resemblance of the transition state to the corresponding cyclopropyl carbonium ion. A very small fraction of the large accelerating effect of a cyclopropyl substituent seen in reactions leading to carbonium ions would be sufficient to explain the rate data available for reactions leading to cyclopropylcarbinyl radicals (3). This paper reports kinetic evidence for a series of decomposition reactions in which acceleration associated with cyclopropyl substituents is not related to cleavage of the cyclopropyl rings and in which transition state charge polarization effects seem to be unimportant.

Overberger and Berenbaum (1 g,h) report the decomposition (80°, toluene) of 2-2'-azobis-2-cyclopropylpropionitrile (Ib) to be twenty times faster than that of azobisisobutyronitrile (AIBN, Ia). Since the only product with cyclopropyl rings intact (III) is formed in only 19% yield in solution decomposition of Ib (4), the possibility remains that all* or most of the observed acceleration could be attributed to a concerted cleavage of C-N and C-C bonds. In

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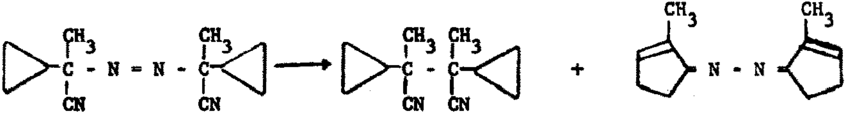
*A three-bond cleavage (similar to that illustrated by V), involving only a single cyclopropane ring, would yield one radical with the cyclopropane ring intact.

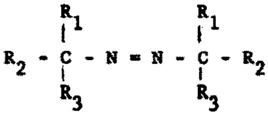
certain other cases acceleration in the rate of formation of cyclopropylcarbinyl radicals is thought to be the result of "manifestations of the ring strain only" (5).



Ib III (19%) IV (7%)

TABLE 1

Decomposition of Azo Compounds



$$R_2-\overset{\overset{R_1}{|}}{\underset{\underset{R_3}{|}}{C}}-N=N-\overset{\overset{R_1}{|}}{\underset{\underset{R_3}{|}}{C}}-R_2$$

In Toluene at 80.2°

Compound	R_1	R_2	R_3	k,sec^{-1} x 10^4	relative rates	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	$\Delta G^{\ddagger}$
Ia	CH_3	CH_3	CN	1.45[a]	1.0	30.7 ± 0.1[a]	10.4 ± 0.2[a]	27.0
Ib	CH_3	*cyclo*-C_3H_5	CN	37.5[b]	25.8	27.7 ± 0.4[b]	8.4 ± 1.2[b]	24.7
Ic	*cyclo*-C_3H_5	*cyclo*-C_3H_5	CN	347[c]	240	23.7 ± 0.7[c]	1.5 ± 2.5[c]	23.2

In Diphenylether at 135.0°

Compound	R_1	R_2	R_3	k,sec^{-1} x 10^4	relative rates	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	$\Delta G^{\ddagger}$
IIa	CH_3	CH_3	CH_3	0.0094	1.0	42.2 ± 0.3[d]	16.2 ± 0.6[d]	35.6
IIb	*cyclo*-C_3H_5	CH_3	CH_3	0.252	26.8	37.8 ± 0.3[e]	12.4 ± 0.6[e]	32.7
IIc	*cyclo*-C_3H_5	*cyclo*-C_3H_5	CH_3	3.41	362	35.6 ± 0.2[f]	12.1 ± 0.6[f]	30.6
IId	*cyclo*-C_3H_5	*cyclo*-C_3H_5	*cyclo*-C_3H_5	23.9	2,540	34.3 ± 0.3[g]	12.8 ± 0.8[g]	29.1
IIe	*cyclo*-C_3H_5	*cyclo*-C_3H_5	*i*-C_3H_7	2.70	286	38.0 ± 0.7[h]	17.6 ± 0.6[h]	30.8

[a] Calculated from data by J. P. Van Hook and A. V. Tobolsky, *J. Am. Chem. Soc.*, *80*, 779 (1958).

[b] Calculated from data in reference 1h.

[c] Calculated from experimentally determined rate constants between 15 and 45°.

[d] Calculated from experimentally determined rate constants between 165 and 200°. Values of 42.3 ± 0.8 for $\Delta H^{\ddagger}$ and 17.5 ± 1.5 for $\Delta S^{\ddagger}$ were obtained from calculations using the gas phase rate constants determined by A. U. Blackham and N. L. Eatough, *J. Am. Chem. Soc.*, *84*, 2922 (1962).

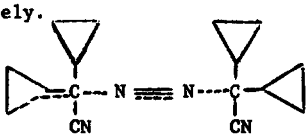
[e] Calculated from experimentally determined rate constants between 145 and 175°.

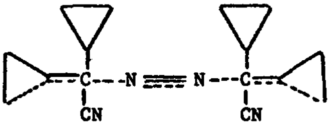
[f] Calculated from experimentally determined rate constants between 120 and 150°.

[g] Calculated from experimentally determined rate constants between 105 and 135°.

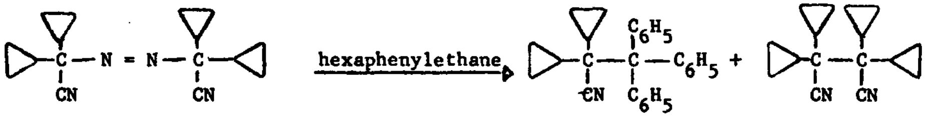
[h] Calculated from experimentally determined rate constants between 120 and 147°.

Results of our studies on the decomposition of Ic show a similar rate acceleration to result from the substitution of a second pair of cyclopropyl groups into the AIBN molecule. If the driving force for the decomposition originates from concerted ring cleavage, then the maximum additional rate acceleration between Ib and Ic would be statistical in origin (a factor of two for a mechanism involving cleavage of one ring, V, or four if two rings were simultaneously involved, VI). The difference between Ib and Ic, 9.3, is greater than the maximum statistical consideration, 4, and makes concerted ring cleavage as the sole provider of the driving force seem unlikely.


V


VI

From the decomposition of Ic in the presence of a slight excess of hexaphenylethane we are able to account for 78% of the material decomposed as reaction products of the dicyclopropylcyanomethyl radical in which both cyclopropyl rings are maintained intact. The products, 2,2-dicyclopropyl-3,3-triphenylpropionitrile (VII, mp 139-140°) and tetracyclopropylsuccinonitrile (VIII, mp 78-79°), were identified from their elemental analyses and infrared and nmr spectra.



Ic VII (53%) VIII (25%)

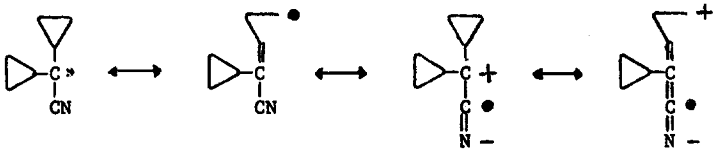
To the extent that decompositions of azonitriles proceed through transition states resembling radical products, the activation energies in Table 1 reflect the stabilizing interaction of cyclopropyl substituents with adjacent radical centers. It can be seen that the effect of replacing each pair of methyl groups with a pair of cyclopropyl groups in the series Ia, Ib, and Ic is roughly additive in free energy. The first pair of cyclopropyl substituents lowers $\Delta G^{\ddagger}$ by 2.3 kcal/mole and the second by 1.5 kcal/mole.

The nature of these interactions might, however, involve charge polarization of two types which would remove electron density from the central carbon atom of the incipient radical in the highly polarizable transition state. The first type, represented by resonance structures IX and X, is of a type expected when a bond joining two atoms of different electronegativity is stretched or when an electronegative atom abstracts hydrogen from a C-H bond (2). This sort of charge polarization is a possible factor in all of the kinetic studies from which arguments have been drawn relative to the stability of cyclopropylcarbinyl radicals. In fact, in several cases where polarization might be expected not to be large, accelerations of radical formation attributable to interactions of cyclopropyl groups are very minor (1a), or essentially undetectable (5). The decompositions of type II azo compounds, thought to proceed by simultaneous cleavage of both C-N bonds (6), presents a case in which symmetry considerations make it seem unlikely that transition state polarization is much greater than ground state polarization. Contributions from structures IX and X place negative charge on adjacent nitrogen atoms and would be mutually delimiting.

$$[R{-}N{=}N{-}R \longleftrightarrow \overset{+}{R}\;\overset{-}{N}{=}N{-}R \longleftrightarrow R{-}N{=}\overset{-}{N}\;\overset{+}{R}]^{\ddagger}$$

IX X

The second type of charge polarization, which might be expected to be present in decomposition of azobisnitriles, is illustrated by resonance structures XIII and XIV. These suggest a possible resemblance of the transition state to the very stable cyclopropyl carbonium ion (3,7). In order to determine the importance of this type of polarization as a possible contributor to accelerations seen for Ib and Ic, we studied the rates of decomposition for a series of azo compounds of type II, lacking the cyano function. Compounds IIa (8); IIb,



XI XII XIII XIV

bp 43-45° (1mm); IIc, bp 80-81° (0.25mm); IId, mp 17-18.5°; and IIe, mp 45.5-46.5°, were prepared by oxidative coupling of the corresponding amines with iodine pentafluoride (8). Complete synthetic procedures will be reported in a later publication. In all cases satisfactory elemental analyses and nmr and infrared spectra were obtained. The decomposition rates were determined in the temperature range 105-200° in diphenyl ether with a small amount of added isoquinoline as a stabilizer against acid-catalyzed decomposition. Again the addition of each pair of cyclopropyl substituents produces an approximately additive change in the free energy of activation. The $\Delta\Delta G^{\ddagger}$ for progression from IIa to IIb is 2.9 kcal/mole; IIb to IIc, 2.1 kcal/mole; and IIc to IId, 1.5 kcal/mole. The deviation from strict linearity in $\Delta G^{\ddagger}$ could be the result of a saturation effect or, more likely, an increasing steric inhibition of resonance as the number of cyclopropyl groups is increased. The close similarity in relative rates and free energy of activation in compounds IIc and IIe provides evidence against a contention that the increase in rate observed in the series IIa, IIb, IIc, and IId is due to an increase in steric repulsion in the ground state that is relieved in the transition state.

Consideration of the data in Table 1 provides an argument against reasoning that acceleration is provided for by relief of ring strain, and the similarity seen in $\Delta\Delta G^{\ddagger}$ values in the two series of Table 1 indicates that the acceleration of decomposition rate seen on substituting cyclopropyl for methyl in an azomethane does not depend on developing carbonium ion character at the central carbon in the transition state, as in XIII or XIV, but reflects a stabilizing interaction between the cyclopropyl substituent and a developing radical center.

Decomposition of 1,1,1,1',1',1'-hexacyclopropylazomethane (IId) in 1,4-cyclohexadiene yields more than 80% of 1,1-dicyclopropyl-1-butene and a small amount (2%) of hexacyclopropylethane. The latter compound was identified by comparison with an authentic sample prepared in 40% yield from photolysis of a sample of IId at 0°.

Hexacyclopropylethane decomposes at 295° in decalin with a first-order rate constant of 1.31×10^{-3} sec^{-1}. This corresponds to a free energy of activation of 41.5 kcal/mole. Using a value of 13 eu for $\Delta S^{\ddagger}$ for the dissociation of hexacyclopropylethane into two tricyclopropylmethyl radicals ($\Delta S^{\ddagger}$ for IId, Table 1), and assuming that (a) solvation effects are unimportant and (b) that the energy of activation for recombination of two tricyclopropylmethyl radicals is small, we arrive at a rough estimate of 45 kcal/mole for the bond dissociation energy of hexacyclopropylethane. The low value of this estimate suggests that decomposition does not proceed by simple cleavage of a cyclopropane ring (9). It is, however, impossible to rule out ring cleavage concerted with central C-C bond cleavage.

The estimate for the bond dissociation energy of hexacyclopropylethane, 45 kcal/mole, while larger than that of hexaphenylethane, 15 kcal/mole, is considerably less than the estimated value of 67.5 kcal/mole for 2,2,3,3-tetramethylbutane (10). These results are consistent with the postulate that tricyclopropylmethyl radicals are resonance stabilized, although the differences in bond dissociation energy may, in part, be attributed to differences in steric interactions.

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