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SUBSTITUENT EFFECTS AND FREE RADICAL STABILITY. THE METHOXY GROUP

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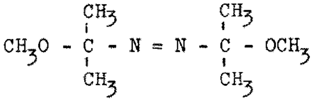
We report a kinetic study which indicates that the stabilizing effect of the methoxy group in a pure radical system is small.

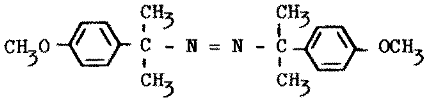
The rates of decomposition of I (diphenyl ether, 150° to 180° C) and II (toluene, 50° to 80° C) were monitored by measuring nitrogen evolution using a constant volume variable pressure kinetic apparatus.[1] The activation parameters,[2] Table I, were calculated from rate constants determined in duplicate at seven different temperatures. The errors are estimated to be $\pm$ 0.2 kcal/mole for Ea and $\Delta H^{\ddagger}$ and $\pm$ 2 e.u. for $\Delta S^{\ddagger}$.

For symmetrical azo compounds like I and II evidence supports decomposition to free radical intermediates by homolytic two bond cleavage.[3,4] Furthermore, since azo compound decompositions to free radical intermediates have relatively large activation energies for bond homolysis, it is likely that the transition states have more radical character than hydrogen abstraction reactions or peroxide decompositions.[5] The entries in Table I, listed in order of increasing relative rate, span a range of 10^6 ($\Delta\Delta G^{\ddagger} = 11$ kcal/mole) in reactivity between X = CH_3 and X = C_6H_5. We believe this difference is too large to be explained by steric considerations. Results obtained for a series of substituted azonitriles (III)[6] where R and R' = methyl, ethyl, isopropyl, and t-butyl support this conclusion. In the azonitrile series the rate varied by less than a factor of 10. It has also been demonstrated that in tertiary substituted azo methanes, replacing a methyl group by a more sterically demanding isopropyl group actually brought about a small decrease in rate of decomposition rather than the expected increase.[1] If we are justified then in ignoring these small ground state energy differences, the rates and activation parameters listed in Table I reflect the stabilizing ability (resonance plus inductive) of a substituent on the free radical center (V), and also allow an assessment of the type of radical produced in azo compound decompositions. If the radical V is considered to be a donor or nucleophilic type radical[13] then in a qualitative sense the rates parallel the ability of a

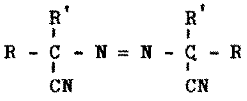


$CH_3O-\underset{CH_3}{\overset{CH_3}{C}}-N=N-\underset{CH_3}{\overset{CH_3}{C}}-OCH_3$

I



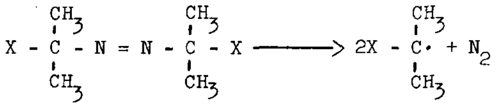
II



$R-\underset{CN}{\overset{R'}{C}}-N=N-\underset{CN}{\overset{R'}{C}}-R$

III

Table I. Activation Parameters for Decomposition of Azomethanes



$$X-\underset{CH_3}{\overset{CH_3}{C}}-N=N-\underset{CH_3}{\overset{CH_3}{C}}-X \longrightarrow 2X-\underset{CH_3}{\overset{CH_3}{C}}\cdot + N_2$$

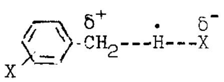
IV V

	Relative Rate 100°	$\Delta G^{\ddagger}$ 100°C	Ea^a kcal mole	log A^a	$\Delta H^{\ddagger a}$ kcal mole	$\Delta S^{\ddagger a}$ eu	Solvent
CH_3	1.0	36.2	43.1	16.9	42.2	16.1	diphenyl ether[1]
$CH_3CH_2CH_2$	2.5	34.5	41.8	16.5	40.9	14.4	hexamethyldecane[7]
CH_3O	10.5	34.3	41.4	17.2	40.5	16.5	diphenyl ether
$C_6H_5CH_2$	16.0	34.1	36.4		35.6	4.1	diphenyl ether[8]
C_6H_5O	50.0	33.2	33.2		32.3	- 2.5	diphenyl ether[8]
Cyclo-C_3H_5	53.0	33.2	38.7	16.1	37.8	12.3	diphenyl ether[1]
C_6H_5S	66.0×10^2	29.6	25.7		24.9	-12.6	diphenyl ether[8]
$CO_2C_2H_5$	25.8×10^4	26.9	29.4	14.3	28.7	4.8	chlorobenzene[9]
CN	29.5×10^4	26.8	31.4	15.5	30.7	10.4	toluene[10]
C_6H_5	41.2×10^5	24.9	29.7	15.7	29.1	11.2	toluene[4,11,12]
P-CH_3O-C_6H_5		24.5	28.3	16.0	27.6	7.8	toluene

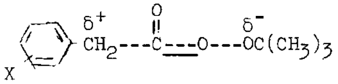
a)Where rate data was available, activation parameters were standardized according to reference 10.

substituent to stablilze an electron sufficient center. This is apparent in that the fastest rates are observed for X=C_6H_5S, $CO_2CH_2CH_3$, CN, and C_6H_5 or those which are carbanion like (electron sufficient) stabilizing groups.

The relatively small difference in rate between X=CH_3 and X=OCH_3, makes it seem unlikely that transition state polarization is a very prominant factor in determining the rate of decomposition of azo compounds like IV. For many free radical systems the Brown equation log $k_x/k_o = \sigma^+\rho$ gives a better correlation than a normal Hammett log $k_x/k_o = \sigma\rho$ treatment.[14] These results are thought to be indicative of a polarized transition state which is stabilized by strongly electron donating substituents. The polarization reflected in the negative ρ values, has been shown to be important for hydrogen abstraction reactions[15,16] (VI) and peroxide decomposition (VII).[17]



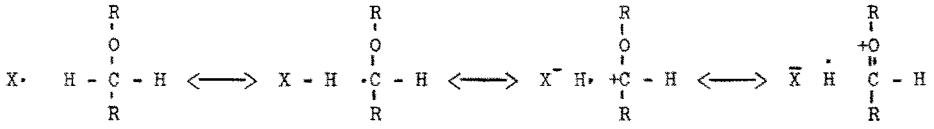
VI



VII

The methoxy group is a substituent with a large negative σ^+ value (-0.78) and is recognized as being an inherently good resonance stabilizing group towards carbonium ion centers. Rates of hydrogen abstraction from ethers[18,19] and calculated[20] stabilization energies of methoxy substituted methyl radicals predict a similar stabilization of radical centers by the methoxy group.

If transition state polarization was a dominant factor in determining the rate of decomposition of azoalkanes a larger rate for $X = OCH_3$ would have been expected. It is possible that the stability commonly associated with ether radicals, as measured by the rate of abstraction of α-hydrogens from ethers, is more a function of the abstracting species that a measure of stability of the intermediate. Abstraction by an electronegative radical (alkoxy,[18] peroxy,[15,19] acyloxy,[21] halogen[22]) provides an additional mode of stabilization (X and XI) by the oxygen atom



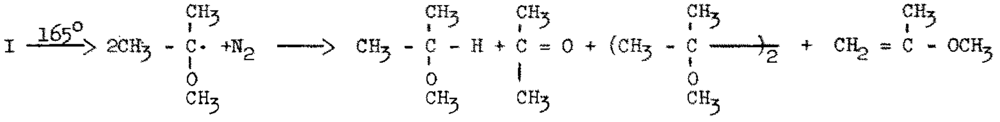
$$X\cdot \quad H-\overset{\overset{R}{|}}{\underset{\underset{R}{|}}{\overset{\overset{O}{|}}{C}}}-H \longleftrightarrow X-H \quad \cdot\overset{\overset{R}{|}}{\underset{\underset{R}{|}}{\overset{\overset{O}{|}}{C}}}-H \longleftrightarrow X^{-}\ H\cdot \ +\overset{\overset{R}{|}}{\underset{\underset{R}{|}}{\overset{\overset{O}{|}}{C}}}-H \longleftrightarrow \bar{X}\ H\ \ \cdot\overset{\overset{R}{|}}{\underset{\underset{R}{|}}{\overset{\overset{+O}{\|}}{C}}}-H$$

VIII IX X XI

in the polarized transition state (VIII - XI).[14]

The substituent effects observed when the X group is shielded from the radical center by a phenyl ring are much less pronounced. Kovacic, Shelton and co-workers[11,12] have evaluated the substituent effects for a series of para substituted azocumenes. Assigning hydrogen the value of 1.00 at 40°C, the following substituent relative rates can be calculated[2] from their data: p-H, 1.00, ($\Delta G^{\ddagger}_{40^{\circ}}$ = 25.6 kcal/mole); p-$C(CH_3)_3$, 0.83, ($\Delta G^{\ddagger}_{40^{\circ}}$ = 25.7 kcal/mole); p-$CH(CH_3)_2$, 0.84, ($\Delta G^{\ddagger}_{40^{\circ}}$ = 25.7 kcal/mole); p-CH_2CH_3, 0.97, ($\Delta G^{\ddagger}_{40^{\circ}}$ = 25.6 kcal/mole); p-F, 1.09, ($\Delta G^{\ddagger}_{40^{\circ}}$ = 25.6 kcal/mole; p-CH_3, 1.33, ($\Delta G^{\ddagger}_{40^{\circ}}$ = 25.4 kcal/mole; m-Cl, 1.89, ($\Delta G^{\ddagger}_{40^{\circ}}$ = 25.2 kcal/mole); p-Br, 2.09, ($\Delta G^{\ddagger}_{40^{\circ}}$ = 25.2 kcal/mole); p-Cl, 2.29, ($\Delta G^{\ddagger}_{40^{\circ}}$ = 25.1 kcal/mole). Our value for p-OCH_3 on the same scale is 2.06, ($\Delta G^{\ddagger}_{40^{\circ}}$ = 25.2 kcal/mole). With the exception of methyl the groups normally thought of as electron donating ($\sigma_I > 0$)[23] are slower than the parent azocumene and those which are electron withdrawing ($\sigma_I < 0$)[23] are faster. However, because of the dilution factor, the extremes X = p-$C(CH_3)_3$ and X = p-Cl differ by less than a factor of 3 ($\Delta\Delta G^{\ddagger}$ = 0.6 kcal/mole), and because no good electron sufficient stabilizing substituents have been evaluated, quantitative comparison between the two systems (IV and azocumenes) is not possible.

The products of decomposition of 1,1'-dimethoxy-2,2'-azopropane (I) were examined by glpc using hexafluorobenzene as an internal standard. The product yields varied only slightly from diphenyl ether to cumene. The significant observation, however, is the similarity in the yield of dimer (XV) and isopropylmethyl ether (XIII) for the two solvents. This indicates that



$$I \xrightarrow{165^{\circ}} 2CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{\overset{|}{O}}}{C}}\cdot + N_2 \longrightarrow CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{\overset{|}{O}}}{C}}-H + \overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}=O + (CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{\overset{|}{O}}}{C}}\longrightarrow)_2 + CH_2=\overset{\overset{CH_3}{|}}{C}-OCH_3$$

XII

	XIII	XIV	XV	XVI
cumene	47%	30%	3%	0.5%
diphenyl ether	41%	27%	4%	trace

cumene doesn't possess any additional ability to scavenge the ether radical (XII) before it can dimerize to give XV, disproportionate to give XIII and XVI or undergo β-scisson to give acetone and methyl radical. Since XVI has limited stability under the reaction conditions, we are unwilling to make statements regarding the absolute fate of XII at this time.

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