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FREE RADICAL-SUBSTITUENT EFFECTS (II),
STERIC EFFECTS AND SULFUR PARTICIPATION

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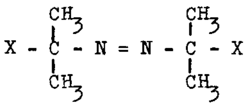
Substituted azopropanes (I) have been shown to be sensitive models for measuring radical-substituent effects.[1] Table I lists relative rates for thermal decompositions that vary by a factor of 10^9 and free energies of activation that differ by as much as 16 kcal/mol. It has been argued[1] that this system is void of contributing transition state polarization[2] making it a purer source of radical than those previously studied.[2] The rates of thermal decomposition of substituted azopropanes can be considered to be the result of resonance, inductive, and steric contributions. Normally models for linear free energy studies have the substituent isolated as far from the reaction site as possible in order to assure minimal steric considerations. This allows evaluation of data in terms of only resonance and inductive effects. It might therefore be argued that 1 is a poor choice as a model because the substituent is directly attached to the incipient radical center and that large steric interactions are present. We advance two arguments which support the contention that the bulk of the rate differences observed in the azopropane series (Table I) are in most cases electronic and not steric. First, the order of increasing radical stability (as measured by rate of formation from azopropanes) parallels that observed in azocumenes (2)[3] and phenylazomethanes (3)[4]. This similarity in the order of substituent effects (H<CH$_3$<CH$_3$O<Cl for 1 and 2 and H<CH$_3$<CH$_3$O<Cl<C$_6$H$_5$ for 1 and 3, Figure 1) implies similar interaction mechanisms, i.e. resonance and inductive. The second point of reference concentrates on compounds 1_c, 1_e, and 1_i of Table I. Little difference in radical stability would be expected (other than small losses in hyperconjugative stabilization) since all three produce tertiary alkyl radicals. The observed rate differences are almost surely steric in origin and examination of models bears this out. The change from methyl (1_c) to t-butyl (1_e), a factor of 12, is



$$X-\underset{CH_3}{\overset{CH_3}{C}}-N=N-\underset{CH_3}{\overset{CH_3}{C}}-X$$

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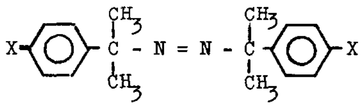

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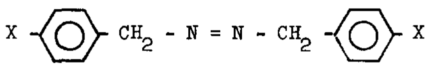

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Table I. Rate Data for Thermolysis of Azopropanes (1)

	X	Relative Rate, 100°C	ΔG*, 100°C kcal/mol	ΔS* e.u.	Reference
a	H	1.0	40.8	17.0	7
b	CH_3CO_2	$2.0x10^2$	36.9	10.3	This work, cf. 8
c	CH_3	$5.6x10^2$	36.2	16.1	9
d	CH_3O	$5.8x10^3$	34.4	16.5	1
e	$(CH_3)_3C$	$7.0x10^3$	34.3	8.3	This work
f	$C_6H_5CH_2$	$8.9x10^3$	34.1	4.1	5
g	C_6H_5O	$2.8x10^4$	33.2	-2.5	5
h	CH_3COS	$3.6x10^5$	31.4	12.7	This work
i	$(CH_3)_3CCH_2$	$7.2x10^5$	30.8	4.0	This work
j	C_6H_5S	$3.7x10^6$	29.6	-12.6	5
k	CH_3S	$1.3x10^7$	28.7	-16.0	This work
l	CN	$1.7x10^8$	26.8	10.4	10
m	C_6H_5	$2.3x10^9$	24.9	11.2	3, 11
n	CH_2=C	$5.0x10^9$	24.3	5.5	12
o	CH≡C	$5.1x10^9$	24.2	8.2	12

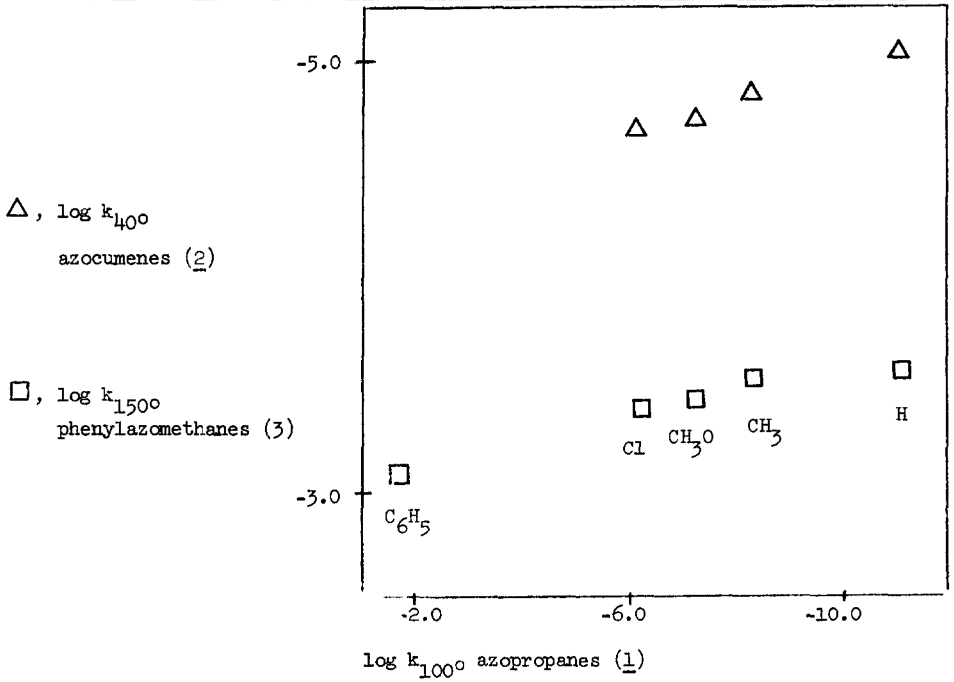
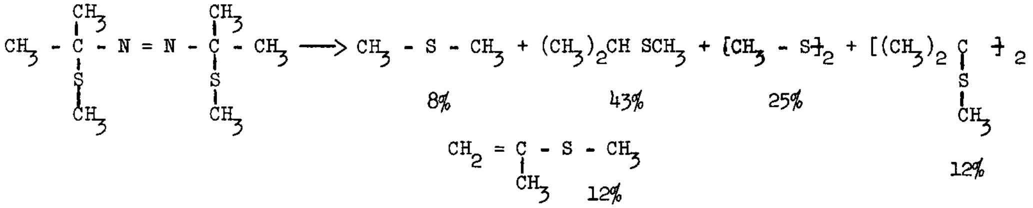


Figure 1

nominal in comparison to the overall change of 10^9. Qualitatively, models predict less steric interference than that of 1_e for all compounds with the exception of 1_i. The latter is interesting in several respects. First, the methyl (1_c) to neopentyl (1_i) change brings about a rate change of 1,300 and shows that if the proper amount of bulk is built into azoalkanes relatively low temperature sources of tertiary alkyl radicals might be accessible. Secondly, this series (1_c, 1_e, 1_i) illustrates the danger involved in trying to quantitatively predict steric effects from ultraviolet absorption maxima. Ohno and Ohnishi[5,6] have used the difference in uv absorption to quantitatively assess differences in energies of ground state vibrational levels. For example, they argue that the rate difference between 1_f and 1_g is accountable from the higher absorption maxima of 1_g (385 nm, compared to 374 nm for 1_f). Applying this uv-steric argument to compounds 1_c (λ_{max} = 368 nm), 1_e (λ_{max} = 376 nm), and 1_i (λ_{max} = 372 nm) would predict 1_e to be the fastest. This is clearly not the case.

Previous work has shown that stabilization by an oxygen atom α to the radical center is small[1,5] ($1_d > 1_c$ by approximately 10). There can be no doubt that the effect of α-sulfur participation is larger. The differences between 1_d and 1_k ($\sim 2.2 \times 10^3$) and 1_b and 1_h ($\sim 1.8 \times 10^3$) are significant and are slightly larger than for the comparison 1_j and 1_g (1.3×10^2) observed by Ohno and Ohnishi. However, there are two facts which force us to be cautious in our interpretation of the results of 1_k (and 1_j). For a fragmentation reaction, like thermolyses of azoalkanes, it is hard to rationalize a large negative entropy of activation. This, and the unusual products of decomposition, points to an unusual mode of decomposition for 1_j and 1_k. The assumed mechanism of decomposition of symmetrically substituted azoalkanes (in solution)



$$CH_3-\underset{\underset{CH_3}{|}}{\underset{S}{|}}{\overset{\overset{CH_3}{|}}{C}}-N=N-\underset{\underset{CH_3}{|}}{\underset{S}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3 \longrightarrow \underset{8\%}{CH_3-S-CH_3} + \underset{43\%}{(CH_3)_2CH\,SCH_3} + \underset{25\%}{[CH_3-S]_2} + \underset{12\%}{[(CH_3)_2\underset{\underset{CH_3}{|}}{\underset{S}{|}}{C}]_2} + \underset{12\%}{CH_2=\underset{CH_3}{\underset{|}{C}}-S-CH_3}$$

is concerted two bond cleavage.[13] Whatever the mechanism of decomposition of 1_j and 1_k, the negative ΔS^* implies a highly ordered, very restricted, transition state. At this time we are not clear as to the actual mechanism. However, the normal ΔS^* and products of decomposition of 1_h (primarily coupling and disproportion) show that the sulfur rate enhancement factor is real.

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13. cf. discussion and references in 1.

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