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Hydrogen Chloride Accelerated Thermal Decomposition of 2,2′-Azoisobutane. Recombination Rate of *tert*-Butyl Radicals[1a]

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Abstract: The effect of HCl on the gas-phase pyrolysis of 2,2′-azoisobutane was studied in a static system over the range 448–462°K. Rate and product analyses, including studies with DCl, reveal that the acceleration is a radical chain process involving H atom abstraction from HCl by thermalized *tert*-butyl radicals and subsequent attack on the azo compound by Cl atoms. The relative rates of the unimolecular decomposition and the chain process provide the rate constant for *tert*-butyl radical recombination. This value at 462°K is $10^{5.6}$ M^{-1} sec^{-1}, lower than the reported value by a factor of $10^{3.9}$, but in excellent agreement with thermochemistry and data for the pyrolysis of hexamethylethane. The thermolysis of 2,2′-azoisobutane produces *tert*-butyl radicals with sufficient excess vibrational energy to provide a significant chain component to the pyrolysis at 460°K. In the present work, possible confusion from all such hot radical effects was eliminated by the use of CO_2 as a moderator.

Interpretation of the kinetics of many reactions involving free radicals is critically dependent on values for the recombination rate constants of the respective radicals. In addition, a great many other rate constants are known only relative to recombination rates. For methyl radicals, it is well known[2–7] that every singlet collision results in recombination; *i.e.*, the Arrhenius *A* factor is equal to ¼ collision frequency and there is no activation energy. [At 400°K collision frequency is given by k (M^{-1} sec^{-1}) $\cong 10^{11.0}$.] For larger alkyl radicals, the situation is less clear. The rate constant for recombination of *tert*-butyl radicals has been reported[8] to be $10^{9.5}$ M^{-1} sec^{-1}, but this value is completely incompatible with the measured rate of the reverse reaction[9] and the "known" thermochemistry, which must relate the two rate constants. The comparison is given briefly below with the pertinent data shown in Table I.

Table I. Data Pertaining to the Reaction

$$(CH_3)_3C{-}C(CH_3)_3 \underset{r}{\overset{-r}{\rightleftarrows}} 2(CH_3)_3C\cdot^{a}$$

			Reaction thermodynamics		
	HMe	$(CH_3)C\cdot$	$\Delta X°_{298}$	$\langle \Delta X°_{700}\rangle^{i}$	$\Delta X°_{1100}$
$\Delta H_f°_{298}$	$-54.0^{b,g}$	7.8 ± 1^{c}	69.6		60.4
$S_f°$	93.1^{h}	75.4 ± 1.0^{d}	57.7		44.6
$C_{p,700}$	89.5^{h}	39.0^{d}		-10.1 ± 2	

Predicted[e] Parameters for Recombination (r)

			460°K	
	1100°K		Loose TS	Tight TS
		$\Delta C_{p_r}{}^{\ddagger}{}_{775}$	-3 ± 2	$+3 \pm 2$
Log $A_r{}^{f}$	8.9		8.8	7.6
$E_r{}^{g}$	9.2		8.5	4.7
Log $k_r{}^{f}$	7.1		4.8	5.4

[a] Log k_{-r} (sec^{-1}, 1100°K) (see ref 9) = $16.3 - 68.5/2.3RT$. [b] All thermodynamic data, unless otherwise noted, are from API Tables, ref 10. [c] Reference 13. [d] Reference 12, slight change in entropy from reference, due to difference in calculated rotational entropy. [e] Calculations outlined in ref 14 and 15b. [f] M^{-1} sec^{-1}. [g] kcal/mol. [h] cal/(mol °K). [i] $(T_2 - T_1)\langle \Delta C_p° \rangle = \int_{T_1}^{T_2} \Delta C_p°\, dT$.

Tsang,[9] using a shock tube technique of demonstrated reliability in measuring Arrhenius parameters for unimolecular decomposition, has investigated the pyrolysis of hexamethylethane. His reported parameters

$$(CH_3)_3C{-}C(CH_3)_3 \underset{r}{\overset{-r}{\rightleftarrows}} 2(CH_3)_3C\cdot$$

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[1] (a) This work was supported in part by Grant No. AP 00353-07 of the Air Pollution Control Administration, Environmental Protection Agency. (b) Postdoctoral Research Associate.

[2] (a) R. Gomer and G. B. Kistiakowsky, *J. Chem. Phys.*, **19**, 85 (1951); (b) H. E. Van Den Berg, A. B. Callear, and R. J. Nordstrom, *Chem. Phys., Lett.*, **4**, 101 (1968).

[3] G. B. Kistiakowsky and E. K. Roberts, *J. Chem. Phys.*, **21**, 1637 (1953).

[4] R. E. March and J. C. Polanyi, *Proc. Roy. Soc., Ser. A*, **273**, 360 (1963).

[5] F. Mosely and J. C. Robb, *ibid.*, **243**, 120 (1957).

[6] N. Basco, D. G. L. James, and R. D. Suart, *Int. J. Chem. Kinet.*, **2**, 215 (1970).

[7] W. Braun, A. M. Bass, and M. Polling, *J. Chem. Phys.*, **52**, 5131 (1970).

[8] E. L. Metcalfe, *J. Chem. Soc.*, 3560 (1963).

[9] W. Tsang, *J. Chem. Phys.*, **44**, 4283 (1966).

for reaction −r at 1100°K are

$$\log k_{-\mathrm{r}}\ (M^{-1}\ \mathrm{sec}^{-1}) = 16.3 - 68.5/\theta$$

where $\theta = 2.303RT$. The heat of formation, entropy, and heat capacity of hexamethylethane are known.[10] Since there is convincing evidence that alkyl radicals are planar,[11] and since systems with sixfolds ymmetry have ~0 barrier to internal rotation, the entropy and heat capacity of the *tert*-butyl radical can be calculated.[12] The heat of formation of the *tert*-butyl radical is known[13] from the kinetics and thermochemistry of iodine atom reactions involving that radical. These values (Table I) give $\Delta H°_{-\mathrm{r},298} = 69.6$ kcal/mol. Since there is in pyrolysis a large decrease in heat capacity [$\langle \Delta C_{\mathrm{p}_{-\mathrm{r},700}} \rangle = -10.1$ cal/(mol °K)], the heat of the reaction will be some 8 kcal/mol less[14] at 1100°K than at 298°K. This gives $\Delta H°_{-\mathrm{r},1100} = 61.5$ kcal/mol. When compared with $\Delta H°^{\ddagger}_{-\mathrm{r},1100} = E_{-\mathrm{r},1100} - RT = 68.5 - 2.2 = 66.\ 3$ kcal/mol, the conclusion required is that, at 1100°K, $\Delta H°^{\ddagger}_{\mathrm{r}} = 4.8$ kcal/mol. Since the Arrhenius activation energy based on concentration unit rate constants corresponds, for a bimolecular reaction, to $\Delta H°^{\ddagger}_{-\mathrm{r}} + 2RT$, it would appear that the activation energy for recombination at 1100°K is in the vicinity of 9.2 kcal/mol.[15a]

The *A* factor for recombination is provided by Tsang's experimental *A* factor for pyrolysis[9] (log $A_{-\mathrm{r},1100}$ (M^{-1} sec^{-1})) together with the net entropy change for the reaction. The value calculated is log $A_{\mathrm{r},1100}$ (M^{-1} sec^{-1}) = 9.4. The temperature dependence of these Arrhenius parameters can be calculated, provided that the heat capacity of activation for recombination, $\Delta C^{\ddagger}_{\mathrm{p}_\mathrm{r}}$, is known. Consideration of the range of possibilities for internal motion in the recombination transition state gives[16] a $\Delta C^{\ddagger}_{\mathrm{p},\mathrm{r},775°}$ of from −3 to +3 cal/(mol °K), with the latter value being the most likely. In either case, as Table I indicates, the Arrhenius parameters at 450°K give a rate constant for recombination of $\sim 10^5$ M^{-1} sec^{-1}, less than the reported value[8] of $10^{9.5}$ M^{-1} sec^{-1} by a factor of more than 10^4. The error limits shown in Table I provide an uncertainty of $10^{1.2}$ in the calculated recombination rate constant but, even were such a large error likely, the discrepancy between the calculated rate constant and the reported value is so great as to warrant some effort at resolution. Consideration of the experimental basis for the latter value[8] suggested that our effort would be best spent on that end of the thermochemical cycle.

Results

The pyrolysis of 2,2′-azoisobutane, with or without HCl, is somewhat complicated, and the experimental values would be difficult to present in a useful way apart from some discussion of their interrelationships. Therefore, in this section the experimental results are presented and their interpretation is discussed in light of the appropriate steady-state analyses. The actual steady-state derivations are presented in Appendixes A and B. In this section we consider, in order: previous studies of azoisobutane pyrolysis; our pyrolysis results and the clarification of the mechanism which they provide; the use of observed pyrolysis stoichiometry to obtain a rough value for k_r; the effect of added HCl on the pyrolysis and the general interpretation of this in terms of the pyrolysis mechanism; and the use of the HCl acceleration, together with other known values, to determine the rate constant for *tert*-butyl radical recombination.

Previous Studies of 2,2′-Azoisobutane Pyrolysis. Levy and Copeland[17] (LC) found the reaction to be more complicated than might be anticipated from the fact that initiation (reaction i, Figure 1) produces only N_2 and two relatively unreactive *tert*-butyl radicals. They observed good first-order kinetics[18] over the temperature range 180–220° (453–493°K); the measured Arrhenius parameters are log *k* (sec^{-1}) = 16.34 − 42.8/2.3*RT*. The reaction products consisted of N_2 (1.0 mol), isobutane (1.34 mol), hexamethylethane (≤0.09 mol), and trace amounts (≤0.03 mol) of isobutylene and methane. The missing carbon (2.0 − 1.34 − 0.18 = 0.48 mol) was found as a polymer coating on the reaction vessel. It was also found that a twofold excess of isobutylene did not change the rate of decomposition of azoisobutane but substantially prevented the formation of polymer.

The authors' interpretation of these results was that abstraction by *tert*-butyl radical of an allylic hydrogen from isobutylene formed in the disproportionation step is competitive with disproportionation (or recombination[19a]) itself. Combination of the allylic radicals produced by this abstraction, and by abstraction from higher molecular weight olefins, continues until an olefin is produced that has insufficient vapor pressure to remain in the gas phase. This mechanism is illustrated by reactions 1–4 in Figure 1. Finally, the authors took good first-order kinetics as evidence against any chain mechanism and the high *A* factor ($10^{16.3}$) as suggestive of simultaneous two-bond rupture.

An alternative mechanism for the consumption of isobutylene which involves successive addition of *tert*-butyl radicals to an olefin is unimportant, since it would result in no excess of isobutane over nitrogen. Allylic hydrogen abstraction by *tert*-butyl radical (reaction 1, Figure 1) thus remains as the most likely pathway for consumption of isobutylene. The striking fact is that a process known from the rates of analogous

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[10] F. D. Rossini, *et al.*, "API Tables," Carnegie Press, Pittsburgh, Pa., 1963.

[11] R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963).

[12] H. E. O'Neal and S. W. Benson, *Int. J. Chem. Kinet.*, **1**, 221 (1969).

[13] D. M. Golden and S. W. Benson, *Chem. Rev.*, **69**, 125 (1969).

[14] S. W. Benson, "Thermochemical Kinetics," Wiley, New York, N. Y., 1968, p 19.

[15] (a) Alternatively, the comparison may be made *via* $\Delta E°_{-\mathrm{r},1100} = 59.3$ kcal/mol and the experimental $E_{-\mathrm{r},1100} = 68.5$ kcal/mol to give $E_{\mathrm{r},1100} = 9.2$ kcal/mol. Note, however, that for a reaction r of mole change $\Delta n = -1$, $E_\mathrm{r} - E_\mathrm{r} = \Delta E°_\mathrm{r}$ only for concentration unit Arrhenius activation energies.[15b] (b) D. M. Golden, *J. Chem. Educ.*, **48**, 235 (1971).

[16] S. W. Benson and H. E. O'Neal, "Kinetic Data on Gas-Phase Unimolecular Reactions," NSRDS, NBS-21, U. S. Government Printing Office, Washington, D. C., 1970, p 25.

[17] J. B. Levy and B. K. W. Copeland, *J. Amer. Chem. Soc.*, **82**, 5314 (1960).

[18] Based on measurements of total pressure.

[19] (a) Throughout this paper we have considered the disproportionation/recombination ratio for the *t*-Bu radical to be 3. This was taken as a likely average of the published values, which can be found in ref 19b and references cited therein. A 10% error in this value would be reflected as a 10% error in the measured recombination rate constant. (b) J. O. Terry and J. H. Futrell, *Can. J. Chem.*, **46**, 664 (1968).

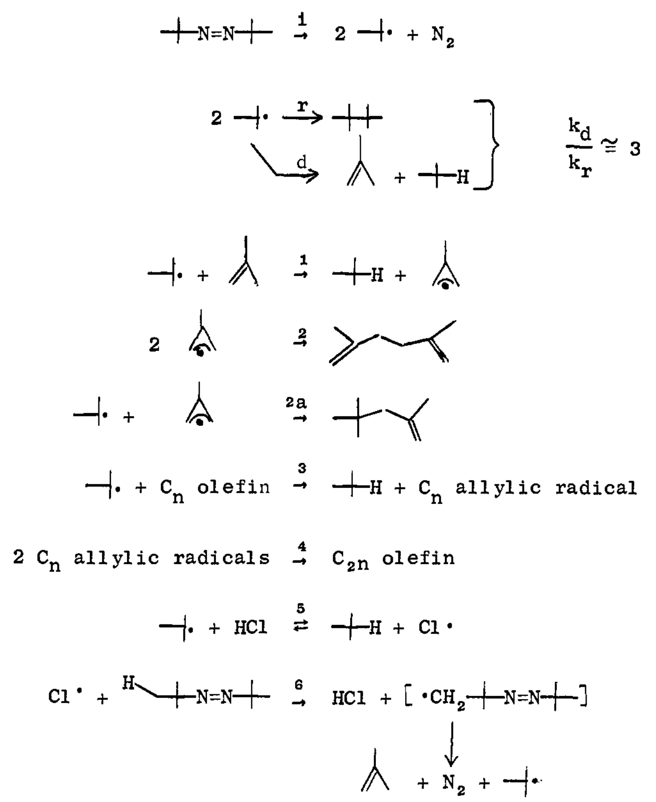


Figure 1. Principal reactions in azoisobutane pyrolysis in the presence of HCl.

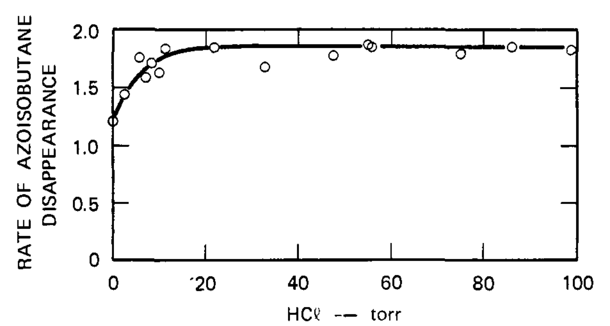
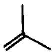


Figure 2. Rate of 2,2′-azoisobutane decomposition as a function of HCl concentration.

reactions[20] to have at least 7 kcal/mol activation energy and an *A* factor corresponding to only one reaction in every thousand collisions of sufficient energy[21] is competing with recombination and disproportionation, processes which are supposed to occur at almost every collision. (In the present pyrolysis experiments, collisions of *tert*-butyl radical with isobutylene are 10^2–10^4 times more frequent than with another *tert*-butyl radical.) A slightly different explanation that would not imply an unexpectedly low recombination rate constant and that cannot be dismissed without further evidence would involve allylic hydrogen abstraction by a vibrationally excited *tert*-butyl radical.

Present Pyrolysis Studies. The results of our rate studies of the pyrolysis of 2,2′-azoisobutane are given, in part, in Table II and in Figure 2. These results are in substantial agreement with those of Levy and Copeland[17] with two significant differences: (1) at low temperatures, 448–462°K (LC temperature range, 453–493°K), and small per cent conversion good first-order kinetics are *not* observed; a plot of log $[A_0/A]$ *vs.* time drops off quite markedly, with the initial slope being as much as twice that corresponding to the rate (and Arrhenius parameters) reported by LC, but approaching the latter value at about 50% conversion; (2) the stoichiometry has been found to vary somewhat with time; initially, the ratio of isobutane to nitrogen is about 1 and slowly increases until at 50% conversion it approaches the 1.34 reported by LC. The initial rapid rate was found to be completely independent of the surface condition of the reaction vessel and to be completely moderated by an excess of CO_2 or SF_6, but much less effectively by a similar excess of H_2. Pyrolysis in the presence of a fivefold excess of CO_2 (over azoisobutane) produced good first-order kinetics with rate constants that correspond very well to LC's parameters and stoichiometry that was constant throughout the reaction with the ratio of isobutane to nitrogen being 1.36. The pyrolysis products, in addition to N_2 (1 mol), *tert*-butane (1.36 mol), and an undetermined yield of polymer, were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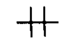
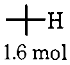
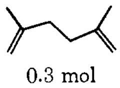
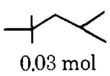
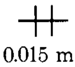


0.02 mol 0.04 mol

In the presence of a 12-fold excess of isobutylene, the products observed were

N_2


1 mol 1.6 mol 0.3 mol 0.03 mol 0.015 mol

Table II. Rates of 2,2′-Azoisobutane Decomposition

Expt	T, °K	$(P_A)_0$	P_{HCl}	P_{CO_2}	P_X	X	$k^1 \times 10^4$ [a]
1	461.4	10.38					1.72[b]
2	461.8	16.70					1.77[b]
3	461.5	10.44			97.4	H_2	1.6
4	461.6	10.47			116	SF_6	1.27
5	461.5	11.46			120	SF_6	1.20
6	461.4	10.44		131			1.18
7	461.5	10.54		57.7			1.30
8	461.6	10.61		21.2			1.38
9	461.9	10.50		62.5			1.22
10	461.9	10.48		132	16.42	=⟨	1.14
11	461.9	11.60	102.4	416	3.04	=⟨	1.22
12	447.9	10.36					0.68[b]
13	447.9	10.41		229			0.31
14	448.0	10.61	77.3	314			0.46
15	460.8	10.75	99.0	327			1.69
16	460.8	10.47	86.0	284			1.70
17	460.8	10.88	74.8	247			1.65
18	461.8	10.43	55.8	284			1.86
19	461.8	10.47	45	149			1.78
20	461.8	10.35	32.8	108			1.67
21	461.8	10.67	21.4	70.5			1.84
22	461.8	10.50	11.05	36.5			1.84
23	461.9	10.59	9.6	152.6			1.63
24	461.9	10.61	8.28	27.3			1.71
25	461.9	10.90	6.51	21.5			1.60
26	461.4	11.00	6.01	34.4			1.66
27	461.0	10.63	2.42	59.2			1.37
28	461.1	10.71	54.9	383			1.77

[a] All k^1 are defined first-order rate constants, *i.e.*, k^1 = the slope of a plot of $-\log(A)$ *vs.* time. [b] For experiments with no moderator, defined rate constant diminishes with time; values listed are calculated at ~25% decomposition.

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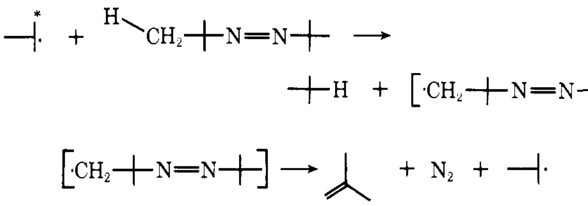
(20) A. F. Trotman-Dickenson and G. S. Milne, NSRDS-NBS-9, U. S. Government Printing Office, Washington, D. C., 1967.

(21) (a) Estimated log k_2 (M^{-1} sec^{-1}) = 7.8 − 7/θ. (b) J. H. Georgakakos, B. S. Rabinovitch, and E. J. McAlduff, *J. Chem. Phys.*, **52**, 2143 (1970).

The moderating effect of a gas that is chemically inert to reaction conditions indicates that species with sufficient excess energy to induce decomposition of the starting material are generated in the course of pyrolyses. In all likelihood, these are vibrationally excited *tert*-butyl radicals produced in the initiating homolysis. It also appears that the induced decomposition proceeds *via* abstraction by a hot *tert*-butyl radical of primary hydrogen from the starting azo compound, analogous to reaction 6, Figure 1.


(1)

It is in the absence of any more obvious explanation that abstraction by excited *tert*-butyl radicals is invoked. With abstraction having an *A* factor that indicates only one effective collision in every one-thousand collisions of sufficient energy, it is difficult to understand[21b] how the excited radical could persist long enough to effect an abstraction.[22] In any event, excess of isobutane and loss of isobutylene continues in the presence of the moderator, so it cannot be claimed that the abstraction of the allylic hydrogens is likewise by hot *tert*-butyl radicals.

As the abstraction-induced decomposition (1) produces one molecule of isobutane and one of nitrogen, it would tend to make the overall stoichiometry nearer to $+\!\!\!\!-\mathrm{H}/\mathrm{N}_2 = 1.0$ than to the 1.35 observed in the completely moderated decomposition. This is, in fact, what was observed. Unfortunately, however, the stoichiometry actually observed in the early stage of the unmoderated decomposition is not a more precise diagnostic for the mechanism of the induced decomposition: excited *tert*-butyl radicals with insufficient energy to cause decomposition of azoisobutane by simple energy transfer have more than enough energy to promote other reactions (*e.g.*, disproportionation), and it would therefore be difficult to extrapolate stoichiometry observed in the moderated system to that expected in the unmoderated system. Nevertheless, for the purposes of the present investigation, the important point is that the results in the moderated pyrolysis all agree with the results of Levy and Copeland and indicate that the mechanism of those authors (reactions i–4 in Figure 1) is correct for the moderated system.

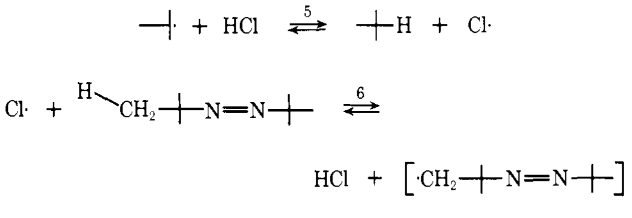
Approximate Measurement of k_r. Given then the validity of the mechanism of reactions i–4 in Figure 1, steady-state analysis allows the use of the stoichiometry observed in moderated azoisobutane pyrolysis as the basis for a rough measurement of the *tert*-butyl radical recombination rate constant. The detailed analysis is included in Appendix A. Briefly, the rationale is that the data require the conclusion that *tert*-butyl radicals (thermalized) disappear by a set of consecutive, competitive reactions: disproportionation (and recombination) to form isobutane and isobutylene (and hexamethylethane), and abstraction of an allylic H from isobutylene (reactions d and r, and 1, respectively, in Figure 1). The isobutylene concentration maintained during pyrolysis depends on which reaction is faster. If the steady-state concentration of isobutylene and the rate of hydrogen abstraction from isobutylene (k_1) are known, these provide, *via* expression 2 (Appendix A), a measure of the recombination rate constant.

$$k_r = (\rangle\!\!=)^2 k_1{}^2/5.1k_i(\mathrm{A}) \tag{2}$$

The value of k_1 has not been measured directly but may be estimated from reported values[20] for analogous reactions. This estimate provides log k_1 (M^{-1} sec^{-1}) = 7.8 − 7 ± $1/\theta$, or $k_1 = 10^{4.5}$ at 462°K. Use of experimental values and equation 2 then gives $k_r = 10^{4.4}$ M^{-1} sec^{-1}, reasonably close to the value of k_r calculated (introduction) from hexamethylethane pyrolysis and thermochemistry.

Pyrolysis in the Presence of HCl. A detailed description of the steady-state analysis connecting the effect of HCl in azoisobutane pyrolysis is contained in Appendix B; a qualitative explanation of that analysis and its application to the present results is given below.

Consideration of reactions 5 and 6 in Figure 1 indicates that, if the concentration of *tert*-butyl radicals is sufficiently high, addition of HCl to the pyrolyzing azo compound should accelerate its decomposition.



If one considers the reaction system only at low per cent conversions, the principal hydrogen donor will be starting material and the acceleration (the rate of reaction 6) will be simply equal to the rate of reaction 5. If (HCl) and k_5 are known, the observed acceleration will be a measure of $(t\text{-Bu}\cdot)_{ss}$. If the dependence of $(t\text{-Bu}\cdot)_{ss}$ on k_r is known, then the acceleration will be a measure of k_r.

As the data in Table II and Figure 2 indicate, HCl, in the presence of a large excess of moderator ($\mathrm{CO_2}$), does indeed accelerate the decomposition of 2,2′-azoisobutane. At low HCl concentrations the acceleration is proportional to (HCl), but at high HCl concentrations the acceleration reaches a limiting value equal to a factor of ~1.5. At high (HCl) the formation of hexamethylethane is completely suppressed and the ratio of isobutane/nitrogen produced is increased very slightly, if at all. When a high concentration of DCl is used, the

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[22] Another explanation of the acceleration has been suggested by a referee: a mechanism whereby an excited *tert*-butyl radical merely transfers energy to a molecule of starting material, upsetting the Boltzman distribution and producing an anomalously high rate of decomposition. Such an explanation is ruled against by the fact that the maximum (estimate subject only, in the case of one-step decomposition, to the estimate of $\Delta H_f°$ of 2,2′-azoisobutane, ref 16, p 457) excess energy a *tert*-butyl radical produced in either a two-step or a one-step decomposition of 2,2′-azoisobutane can have is 36 kcal/mol. If, for every molecule of azoisobutane that is thermally decomposed, another molecule is energized to within 6 kcal/mol of the energy required for activation, the effect on the decomposition rate would be scarcely noticeable. That is, all but a very small fraction of such molecules will lose this energy by collision rather than gaining the extra 6 kcal necessary for reaction. The authors would be happy to hear other alternatives readers might suggest.

isobutane formed in the first 40% of reaction is found to consist of slightly more than 50% $(CH_3)_3C{-}D$, and the unreacted azo compound contains no deuterium.[23] It also appears that the limiting acceleration is temperature independent. At a temperature at which the pyrolysis rate is four times slower, a high HCl concentration still accelerates the decomposition by a factor of ~1.5.

The results of the DCl experiment are necessary, if not sufficient, evidence for the postulated radical chain mechanism of acceleration (reactions 5 and 6 in Figure 1). There is no obvious alternative mechanism that fits the facts; it is difficult to imagine a molecular process (direct reaction of DCl and *t*-Bu-N=N-*t*-Bu) that would result in placing a D in the tertiary position of isobutane. Moreover, if the acceleration were a bimolecular reaction, its rate would, under all conditions, be proportional to HCl concentration.[24] Finally, in order for a bimolecular process involving 100 Torr ($3.5 \times 10^{-3}\,M$ at 462°K) of HCl to be competitive with unimolecular decomposition, the bimolecular process would have to have a much lower activation energy than unimolecular decomposition. That is, the acceleration, contrary to our observations, would be highly temperature dependent.

It is somewhat less obvious that our mechanism predicts the type of HCl dependence the acceleration exhibits (Figure 2). That, in fact, it does is demonstrated by the steady-state analysis in Appendix B but can be seen in a qualitative way by considering the reactions in Figure 1.

The added HCl does not *directly* affect $(t\text{-Bu}\cdot)_{ss}$, since reaction 6 follows rapidly on reaction 5 and replaces the *tert*-butyl radical used in reaction 5. Therefore, since the mechanism requires acceleration to be proportional to the rate of reaction 5, a constant $(t\text{-Bu}\cdot)_{ss}$ would mean that acceleration would be simply proportional to (HCl). However, $(t\text{-Bu}\cdot)_{ss}$ is, in fact, indirectly affected by reactions 5 and 6; reaction 6 produces isobutylene, and isobutylene is a competitor for $t\text{-Bu}\cdot$ (reaction 1). As long as reaction with the isobutylene produced by reaction 6 accounts for only a small portion of the total rate of disappearance of $t\text{-Bu}\cdot$, the $(t\text{-Bu}\cdot)_{ss}$ will be effectively independent of (HCl) and the acceleration should be linearly dependent on (HCl). As the (HCl) increases, however, it is obvious that at some point there will be a significant decrease in $(t\text{-Bu}\cdot)_{ss}$ and some additional increment of HCl will not produce the acceleration it did at lower concentrations. Therefore, acceleration cannot remain proportional to (HCl), and it is not unreasonable that it should approach some constant value. The expression, derived in Appendix B, which describes such a dependence is

$$-\frac{\mathrm{d(A)}}{\mathrm{d}t} = k_1(\mathrm{A}) + k_5(\mathrm{HCl})\left[\frac{[28k_1k_r(\mathrm{A}) + k_5{}^2(\mathrm{HCl})^2]^{1/2} - k_5(\mathrm{HCl})}{14k_r}\right] \quad (3)$$

In the limit of low HCl concentration, this expression reduces to

$$-\frac{\mathrm{d(A)}}{\mathrm{d}t} = k_1(\mathrm{A}) + k_5(\mathrm{HCl})\left(\frac{k_1(\mathrm{A})}{7k_r}\right)^{1/2} \quad (4)$$

and at high HCl to

$$-\mathrm{d(A)}/\mathrm{d}t = k_1(\mathrm{A}) + k_1(\mathrm{A}) = 2k_1(\mathrm{A}) \quad (5)$$

Further consideration of the reactions in Figure 1, together with the fact that the products contain almost no isobutylene, amplifies the meaning of expressions 3–5. High HCl concentration, since it lowers $t\text{-(Bu}\cdot)_{ss}$, will cause all reactions second order in *tert*-butyl radical to decrease relative to reactions that are first order in *tert*-butyl radical. Since reactions 1 and 5 (together with 6) are first order in *tert*-butyl radical and consume and produce, respectively, isobutylene, it can be seen that at high HCl concentration there should be a balance between the two processes. That is, in the limit of high (HCl) the observed acceleration should be independent of the rate of any process second order in $(t\text{-Bu}\cdot)$ and dependent merely on the stoichiometry of the first-order reactions which consume and produce isobutylene. This stoichiometry (see Figure 1) is: reaction 1, which requires one *tert*-butyl radical, also uses one isobutylene; at the same time (see Appendix A), reaction 3 uses one *tert*-butyl radical; and reactions 5 and 6 together bring about no net consumption of *tert*-butyl radicals but produce one isobutylene. Therefore, for every two *tert*-butyl radicals consumed, there must be one induced decomposition or one unimolecular decomposition for every induced decomposition.

There are two things that are likely to make the acceleration (observed factor 1.55) less than the factor of 2.0 thus predicted. To the extent that cross disproportionation (7)

which produces isobutylene is significant, the stoichiometric requirement for induced decompositions as the primary source of isobutylene will be reduced. (If reaction 7 were to amount to, say, 10% of reaction 1, then the acceleration factor would be only 1.75.)

The second likely cause of an acceleration factor less than 2 arises from the fact that whereas the steady-state calculations were made for 0% decomposition, the actual rate measurements were made over substantial percentage reaction. Hydrogen abstraction from starting material (acceleration) by chlorine atoms will be reduced by whatever percentage of the total hydrogen atom supply is comprised by products. Rates of azoisobutane disappearance were measured over the range 20–40% reaction; an observed factor of 1.55 should, therefore, extrapolate to 1.8 at 0% reaction, and the measured acceleration was accordingly increased by 30% (such a correction results in a 30% decrease in the final value of k_r).

The observation that the isobutane/nitrogen ratio is almost independent of (HCl) is also easily explained. The mechanism (Figure 1) provides that, whether HCl is present or not, the path by which isobutylene and higher olefins are removed from the gas phase is the same: allylic H abstraction by thermal *tert*-butyl radi-

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[23] The absence of deuterium in recovered starting material means that the intermediate radical, $(CH_3)_3CN{=}NC(CH_3)_2CH_2\cdot$, decomposes more rapidly than it reacts with DCl. Assuming an *A* factor of $\sim 10^{-14}$ sec^{-1} for the decomposition of the intermediate, this allows an upper limit of 17 kcal/mol to be placed on the activation energy for that reaction. The actual value is probably much less than this, since the overall reaction is 16 kcal exothermic.

[24] This is true unless there were a bimolecularly formed intermediate whose formation could be reversed.

cals, followed by recombination of the allylic radicals, etc. Also, the stoichiometry of production of isobutane and isobutylene is the same, regardless of whether they are produced by reactions i and d (Figure 1), or by reactions 5 and 6. The only difference that HCl makes in the product stoichiometry results from the fact that the recombination of *tert*-butyl radicals, as a bimolecular reaction, is no longer competitive with reactions first order in *tert*-butyl radical (1, 3, 5). The relatively small number of radicals that would have formed the *tert*-butyl dimer have now formed either polymer or isobutane and have increased the total amount of those two products, but only by a few per cent.

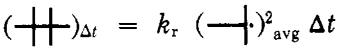
In short, all observations in the HCl accelerated pyrolysis are consistent with the anticipated mechanism (Figure 1) and expression 3. Rearrangement of expression 3 shows that at low HCl concentrations k_r is given by

$$k_r = k_1(\mathrm{A})k_5{}^2(\mathrm{HCl})^2/7[\mathrm{d(A)/d}t - k_1(\mathrm{A})] \qquad (6)$$

The data in Figure 2, *via* expression 6, give $k_r = 10^{5.6}$ M^{-1} sec^{-1} at 462°K. Since k_r depends on the square of k_5, it will be very sensitive to errors in the latter value. The value of k_5 has not been measured directly but is known from the rates of many very consistent measurements of hydrogen abstraction by chlorine[23] and from the equilibrium constant for reaction 3, which is provided by thermochemistry.[10,12,13] The greatest uncertainty in the latter value arises from a 1 kcal/mol uncertainty with heat of formation of the *tert*-butyl radical. The likely error in the entropy of the radical, taken to be that associated with a barrier to methyl rotation as high as 2 kcal/mol (1 gibbs/mol), is much less significant. These errors, when added vectorially to estimated errors in our rate measurements, produce an uncertainty in the final value of k_r of 1.2 powers of ten. Therefore, from a measured value of $k_r = 10^{5.6}$ M^{-1} sec^{-1}, it is possible that the actual value of the *tert*-butyl radical recombination rate constant is as high as $10^{6.8}$ M^{-1} sec^{-1} but highly unlikely that it is anywhere near $10^{9.5}$ M^{-1} sec^{-1}.

It might occur to one at this point that any value based on steady-state analysis of such a complicated system must be considered very tenuous. Such caution is well taken; however, in the present case, there is additional evidence to support our analysis. Whereas in rotating sector "rate" measurements,[25] the assumption is sometimes arbitrarily made that the higher than first-order process which is controlling alkyl radical steady-state concentration is necessarily recombination and disproportionation of two alkyl radicals, in the present case, the following considerations indicate that the assumed modes of radical disappearance are correct.

Whatever the exact stoichiometry, our general mechanism for acceleration (reactions 5 and 6 in Figure 1) requires that the amount of acceleration observed be a direct measure of the steady-state concentration of *tert*-butyl radicals. If the analysis which has related this steady-state concentration to k_r is correct, then the value of k_r extracted must be consistent with the amount of recombination product, hexamethylethane, actually formed. That is, the concentration of hexamethylethane formed in time Δt must equal the average rate of formation multiplied by Δt.



Although the small amount of hexamethylethane formed could be measured with only limited accuracy, it, together with the *tert*-butyl radical steady-state concentration required by the observed acceleration, gives a recombination rate constant $k_r = 9 \times 10^4$ M^{-1} sec^{-1}.

Given the experimental uncertainties, a factor of 4 difference between this value and the one based on the steady-state analysis is not of great significance. However, the direction of the difference makes still another suggestion that our understanding of the mechanism is essentially correct.

As discussed above, our analysis (Appendixes A and B) has assumed that cross combination between *tert*-butyl and allylic radicals is relatively unimportant. To the extent, therefore, that such cross combinations are important termination steps, this analysis will suggest that recombination (and disproportionation) itself is more effective at reducing the *tert*-butyl radical steady-state concentration than it actually is. That is, the calculation based on the steady-state analysis should, if anything, overestimate the value of k_r and, in fact, that calculation does provide a value larger than the one derived from product measurement.

In summary, the only reasonable conclusion that can be drawn from the present results is that the $10^{9.5}$ M^{-1} sec^{-1} reported[8] for the rate constant for *tert*-butyl radical recombination is grossly in error, that the actual value is in all probability much closer to the presently measured $10^{5.6}$ M^{-1} sec^{-1}. Unfortunately, both the accuracy and accessible temperature range of the present method are sufficiently limited so as to preclude any meaningful measure of the activation energy for recombination. However, the question is of such importance that experiments are under way in the authors' laboratory which, together with the present results, will hopefully provide values for the recombination rate constant over a very wide temperature range.

Discussion

The factor of 10^4 discrepancy in the hexamethylethane–*tert*-butyl radical pyrolysis–recombination thermochemical cycle outlined in the introduction would appear to be very nicely resolved by the present result. In addition, the measurement of an alkyl radical recombination rate much slower than collision frequency should be another step on the way to a better understanding of reactions involving such radicals.

The first question the present result prompts is, of course, what makes *tert*-butyl radical recombination slower than collision frequency by a factor of 10^5? The hexamethylethane pyrolysis parameters and thermochemistry (see introduction) suggest that the slower rate is partly the result of a lower A factor but is principally due to an actual activation energy for re-

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[25] In addition to the gas-phase result quoted earlier,[8] several measurements of *tert*-butyl radical recombination rates in solution have been made, and these rates have been reported[26,27] to be nearly diffusion controlled. There is little comment to make except to reiterate that it is dangerous to assume in a complicated reaction system that a change in rate associated with a change in sector speed necessarily depends on the particular second-order termination process one wishes it to, and that this would seem particularly true in the absence of any identification of the actual termination products.

[26] D. J. Carlson and K. U. Ingold, *J. Amer. Chem. Soc.*, **90**, 7047 (1968).

[27] G. S. Hammond and S. A. Weiner, *ibid.*, **90**, 1659 (1968).

combination. That the slower rate be reflected in both parameters is quite reasonable since a recombination activation energy necessarily means a tighter transition state and therefore a lower *A* factor. An activation energy for joining two bulky planar radicals seems, in turn, not unreasonable.

At this point, any further understanding of the detailed origin of the activation energy is difficult, but there is one observation worthwhile making. If a certain amount of steric repulsion results from bringing one *tert*-butyl radical up against another, one might be inclined to guess that the repulsion resulting from the approach of a methyl to a *tert*-butyl radical would not only be less than that amount, but significantly less than half. That is, the repulsion might well not be additive. If that is true, then one would expect that the root-mean-square rule for estimating cross-recombination rate constants $(k_{r_{ab}}) = 2(k_{r_{aa}}k_{r_{bb}})^{1/2}$ would not be followed, and that the methyl–*tert*-butyl recombination rate would be closer (by more than the statistical factor of 2) to the methyl–methyl rate than to the *tert*-butyl–*tert*-butyl rate. In fact, well measured Arrhenius parameters for neopentane pyrolysis,[28] together with thermochemical data,[10,13] require a cross-combination activation energy (M^{-1} sec^{-1} units, 460°K) of 2.5 kcal/mol, a value disturbingly close to halfway between the 4.7 kcal/mol calculated in a similar manner for *tert*-butyl recombination (introduction) and the 0 kcal/mol value for methyl radicals. The meaningfulness of the calculations is supported by the fact that product measurements in systems containing various radicals also indicate that the root-mean-square rule is generally obeyed.[29] Thus it would appear, contrary to what one might have suspected, that the recombination activation energy is not the result only of repulsions between two bulky tertiary radicals but is characteristic of the process of forming any carbon–carbon bond to a tertiary center. It is hoped that work currently underway in our laboratory will shed more light, not only on the absolute values of these rates, but also on the detailed nature of the recombination process.

Experimental Section

Materials. The 2,2′-azoisobutane was supplied by Merck Sharpe and Dohme of Canada. It was used as received (≥99% pure by vpc) except for degassing and bulb-to-bulb distillation. Storage in the dark prevented measurable decomposition. CO_2 was Matheson bone dry, degassed.

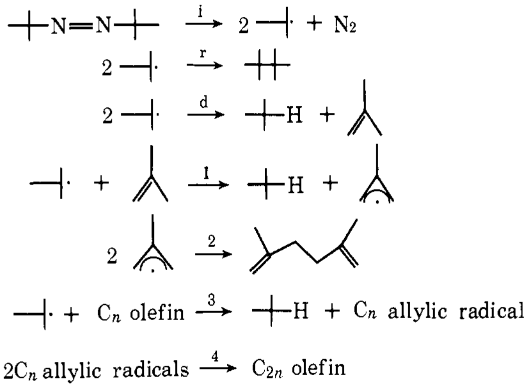
Authentic product samples for vpc and mass spectral comparison were obtained from Phillips Petroleum, Aldrich Chemical Co., and Chemical Samples, Inc.

Procedure. Reactions were carried out in a static system consisting of a 1-l. cylindrical Pyrex vessel encased in a thermostatically controlled aluminum block oven. Rate measurements were made by vpc sampling, direct from the vessel by way of a glass gas-sampling valve. The use of either a molecular sieve (5A, 5 ft × 0.25 in.) or a diethylhexyl sebacate (on Chromosorb W 80–100, 10 ft × 0.25 in.) column with either liquid nitrogen trapping or an ascarite-packed precolumn made it possible to follow pressure changes of the starting material and of most gaseous products. Reaction products were identified by peak enhancement with authentic samples when possible, and by mass spectral analyses using a coupled vpc–Finnigan quadrupole mass spectrometer.

In no case could any nitrogen-containing products, other than molecular nitrogen, be detected, so N_2 evolved was used as a measure of reaction progress. In pyrolysis itself, N_2 and isobutane were the only major, and isobutylene and hexamethylethane, the only significant minor gaseous products. When the pyrolysis was carried out in the presence of excess isobutylene, the additional significant minor products produced were 2,5-dimethyl-1,5-hexadiene and 2,2,4-trimethylpentane. No cross-combination product, 2,2,4-trimethylpentene-1, could be detected but could well have been masked by starting material, since the two have almost identical retention times on the column used.

Appendix A

Steady-State Analysis of the Pyrolysis of 2,2′-Azoisobutane. If the polymer were to consist principally of C_{64} olefin, the overall stoichiometry required to produce one polymer molecule, according to the mechanism outlined by the reactions below, would include formation of 16 isobutylenes and a total of 30 abstractions from isobutylene and higher olefins. That is, ~2 abstractions are required before the carbons comprising each original isobutylene are no longer in the gas phase in the form of some olefin. Since the overall rate of hydrogen abstraction from one >C–C–< will not be greatly different than abstraction from two isobutylenes, reactions 1 and 3 can, as a first approximation, be replaced simply by reaction 1, where isobutylene is now a generalized olefin whose removal from the gas phase requires two abstractions. The steady-state analysis is then as follows



$$\frac{d(i\text{-}C_4H_8)}{dt} = 0 = k_d(t\text{-Bu}\cdot)^2 - {}^1\!/_2 k_1(t\text{-Bu}\cdot)(i\text{-}C_4H_8)$$

$$(i\text{-}C_4H_8)_{ss} = 2k_d(t\text{-Bu}\cdot)/k_1 \qquad (7)$$

$$\frac{d(t\text{-Bu}\cdot)}{dt} = 0 = 2k_i(A) - 2(k_r + k_d)(t\text{-Bu}\cdot)^2 - k_1(t\text{-Bu}\cdot)(i\text{-}C_4H_8)$$

$$(t\text{-Bu}\cdot)_{ss} = \left[\frac{2k_i(A)}{2(k_r + k_d) + k_1(i\text{-}C_4H_8)/(t\text{-Bu}\cdot)}\right]^{1/2} \qquad (8)$$

Substituting (7) into (8)

$$(t\text{-Bu}\cdot)_{ss} = \left[\frac{2k_i(A)}{2(k_r + k_d) + \dfrac{k_1 2k_d(t\text{-Bu}\cdot)}{(t\text{-Bu}\cdot)k_1}}\right]^{1/2} = \left[\frac{k_i(A)}{k_r + 2k_d}\right]^{1/2}$$

Since $k_d \cong 3k_r$

$$(t\text{-Bu}\cdot)_{ss} = [k_i(A)/7k_r]^{1/2} \qquad (9)$$

Substituting (9) into (7)

$$(i\text{-}C_4H_8)_{ss} = \frac{6k_r}{k_1}\left[\frac{k_i(A)}{7k_r}\right]^{1/2} = \left[\frac{36k_r k_i(A)}{7k_1}\right]^{1/2}$$

$$k_r = (i\text{-}C_4H_8)_{ss}{}^2 k_1{}^2/5.15k_i(A)$$

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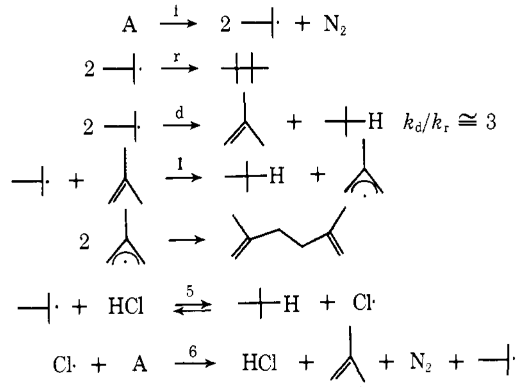
[28] W. Tsang, *Int. J. Chem. Kinet.*, 1, 245 (1969).

[29] J. A. Kerr and A. F. Trotman-Dickenson, *Progr. React. Kinet.*, 1, 105 (1961).

Appendix B

Steady-State Analysis of HCl Accelerated 2,2′-Azoisobutane Pyrolysis. The mechanism change from that invoked in Appendix A is changed only by the addition of reactions 5 and 6.



Since, in early stages of reaction, the rate of reaction 6 will be simply equal to the rate of reaction 5

$$\frac{d(i\text{-}C_4H_8)}{dt} = 0 = k_d(t\text{-Bu}\cdot)^2 + k_5(t\text{-Bu}\cdot)(\text{HCl}) - {}^1/_2k_1(t\text{-Bu}\cdot)(i\text{-}C_4H_8)$$

$$(i\text{-}C_4H_8)_{ss} = \frac{2k_d(t\text{-Bu}\cdot) + 2k_5(\text{HCl})}{k_1} \qquad (1)$$

$$\frac{d(t\text{-Bu}\cdot)}{dt} = 2k_1(\text{A}) - 2(k_r + k_d)\,(t\text{-Bu}\cdot)^2 - k_1(t\text{-Bu}\cdot)(i\text{-}C_4H_8)$$

$$(t\text{-Bu}\cdot)_{ss} = \left[\frac{2k_1(\text{A})}{2(k_r + k_d) + k_1\dfrac{(i\text{-}C_4H_8)}{(t\text{-Bu}\cdot)}}\right]^{1/2} \qquad (2)$$

Substituting (1) in (2)

$$(t\text{-Bu}\cdot)_{ss} = \left[\frac{2k_1(\text{A})}{2(k_r + k_d) + \dfrac{2k_1[k_d(t\text{-Bu}\cdot) + k_5(\text{HCl})]}{(t\text{-Bu}\cdot)k_1}}\right]^{1/2}$$

$$(t\text{-Bu}\cdot)_{ss} = \left[\frac{k_1(\text{A})}{k_r + 2k_d + \dfrac{k_5(\text{HCl})}{(t\text{-Bu}\cdot)}}\right]^{1/2}$$

$$(t\text{-Bu}\cdot)_{ss}{}^2(7k_r) + k_5(\text{HCl})(t\text{-Bu}\cdot) - k_1(\text{A}) = 0$$

$$(t\text{-Bu}\cdot)_{ss} = \frac{-k_5(\text{HCl}) \pm [k_5{}^2(\text{HCl})^2 + 28k_rk_1(\text{A})]^{1/2}}{14k_r}$$

Since the acceleration corresponds to the rate of reaction 5, the total rate of azobutane decomposition will be given by

$$\left(-\frac{d(\text{A})}{dt}\right)_{\text{HCl}} = k_1(\text{A}) + k_5(\text{HCl})(t\text{-Bu}\cdot)$$

$$\left(-\frac{d(\text{A})}{dt}\right)_{\text{HCl}} = k_1(\text{A}) + k_5(\text{HCl})\left[\frac{[k_5{}^2(\text{HCl})^2 + 28k_rk_1(\text{A})]^{1/2} - k_5(\text{HCl})}{14k_r}\right]$$

Rate–Equilibria Relationships and Proton-Transfer Reactions

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Abstract: In view of the central role that Hammond's postulate has played in the attempt to correlate structural variations and chemical reactivity, it would be desirable to extend this concept beyond its qualitative nature. This has now been accomplished. From a derivation based on Hammond's postulate, equations are obtained that relate the free-energy barrier of a reaction to ΔF and the barrier height at $\Delta F = 0$ ($\Delta F_0{}^*$). The final equations are identical with those originally developed by Marcus for electron-transfer reactions. Using these results, rate constants (k_b and k_{-b}) are calculated for the forward and reverse directions of a simple one-step proton-transfer reaction, where $\alpha = d \log k_b/d \log (k_b/k_{-b})$. The rate constants k_b and k_{-b} are incorporated into a multistep mechanism for proton transfer, and the "observed" rate constants k_{for} and k_{rev} are calculated. The "experimental" Brønsted coefficient, $\alpha_{exp} = d \log k_{for}/d \log (k_{for}/k_{rev})$, is computed. A comparison of α and α_{exp} allows a test of the frequently invoked assumption that an experimental Brønsted coefficient is a true indicator of transition state structure. Results are obtained which show that even when Hammond's postulate is obeyed, α_{exp} is not always reliable for predicting the position of the transition state along the reaction coordinate.

The Brønsted equation has been applied to a wide variety of reactions including general acid and general base catalysis,[2a] nucleophilic catalysis,[2b] and proton exchange reactions. These latter reactions have involved not only oxygen, nitrogen, and sulfur acids[3] but also carbon acids, including nitroalkanes,[4] cyanocarbons,[5] ketones,[6] sulfones,[7] and hydrocarbons.[8]

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[3] M. Eigen, *Angew. Chem., Int. Ed. Engl.*, **3**, 1 (1964).

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