98. Rates of Proton Abstraction from Conjugated Dienes in the Gas Phase

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Summary

The rates of proton transfer from 2,4-hexadiene, 1,3-cycloheptadiene, cyclopentadiene and acetone to *t*-butoxide have been measured in the gas phase using pulsed-ion-cyclotron-resonance spectroscopy. The rate constants are (units of 10^{-10} cm^3 molecule^{-1} s^{-1}): 2.7 ± 0.4, 3.8 ± 0.4, 6.1 ± 0.7 and 10.8 ± 1.5, respectively. These results are analyzed in terms of the properties of the encounter complex and reaction transition states. The reaction profile for *t*-butoxide + cyclopentadiene is modeled using RRKM theory and an estimate for the central barrier height is obtained.

Introduction. – Owing to their fundamental importance in solution chemistry, proton transfer reactions in the gas phase have been studied extensively using pulsed-ion-cyclotron-resonance spectrometry, flowing afterglow, and high-pressure mass spectrometry. The general trend which has emerged is that proton transfers between two localized ions such as alkoxides proceed with rates close to collision-controlled [1], whereas those between delocalized anions such as enolates can be quite slow even when appreciably exothermic [2]. *Bartmess, Scott & McIver* suggest [3] that intermediate rates will be found for reactions that involve either a localized negative ion and delocalized CH acid or two delocalized OH or NH acids. We give some examples that this is indeed the case by reporting here some rate constants for the reactions of *t*-butoxide anion with various CH acids.

We have developed a general model for ion-molecule reactions which utilizes a double minimum potential surface as described in Fig. 1 [2] [4] [5]. RRKM calculations can be used to estimate the central barrier height [4] [5]. A similar approach is taken here and a barrier height is calculated for the reaction of *t*-butoxide with cyclopentadiene. The choice of open and cyclic dienes as well as acetone for comparison allows us to discuss the results in terms of entropy and overall enthalpy effects on the transition state.

Experimental Part

Instrumentation. Rate constants were measured using a pulsed-ion-cyclotron-resonance spectrometer equipped with a trapped ion cell [6]. The marginal oscillator frequency employed was 153 kHz. Total

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pressures were 10^{-7}–10^{-5} Torr, measured with a *Varian UHV-24* ionization gauge calibrated in the 10^{-5}–10^{-4} Torr range against an MKS *Baratron* (170M-6B) capacitance manometer. Ionization gauge-*Baratron* readings were linear in this range; the *Baratron* readings were calibrated periodically against the rate constant of $1.1 \pm 0.1 \times 10^{-9}$ cm³ molecule⁻¹ s⁻¹ for the reaction $CH_4^+ + CH_4 \rightarrow CH_5^+ + CH_3$ [7].

Determination of Rate Constants. t-Butoxide ions were generated by electron impact (1–2 eV) on di-*t*-butyl peroxide at pressures of ~ 10^{-7} Torr. The ions were scanned over time to check for adequate trapping and the absence of unwanted side reactions, and then a known pressure of reactant gas was added. The pseudo-first-order decay of the reactant ion was recorded, and the rate constant was determined from this trace and the reactant gas pressure. The rate constants reported in *Table 1* are the mean and standard deviations of more than 15 runs on two different days.

Materials. Di-*t*-butyl peroxide (MCB), (2*Z*, 4*E*)-hexadiene *(Columbia)*, 1,3-cycloheptadiene *(Aldrich)*, and acetone *(Baker)* were obtained commercially and used without further purification. Dicyclopentadiene *(Allied)* was freshly cracked before each experiment.

Results. – The relevant experimental data are shown in *Table 1*. Ion-molecule collision-rate constants used in determining reaction efficiencies were calculated using *Langevin* theory [8], except for the reaction with acetone where average dipole orientation (ADO) theory [8] was used. Reliability of the measured rate constants can be estimated to be about ± 30% due primarily to uncertainty in the *Baratron* readings below 10^{-4} Torr.

Enthalpy changes given in *Table 1* were calculated using data from [3], except for the cases involving 2,4-hexadiene and 1,3-cycloheptadiene for which no gas-phase acidity data are available. For these reactions, the required acidities were estimated from the relative values for cyclopentadiene and 1,3-pentadiene [9].

Table 1. *Rate constants, reaction efficiencies and reaction enthalpies of the proton abstraction of conjugate dienes and acetone by t-BuO⁻ in the gas-phase*

Reaction	Rate Constant $k_H \times 10^{10}$ cm³ molecule⁻¹s⁻¹	Reaction efficiency[b]	ΔH° kcal mol⁻¹
t-BuO⁻ + 2,4-hexadiene	2.7 ± 0.4[a]	0.21 ± 0.03	−10[c]
t-BuO⁻ + cycloheptadiene	3.8 ± 0.4	0.29 ± 0.03	−10[c]
t-BuO⁻ + cyclopentadiene	6.1 ± 0.7	0.52 ± 0.06	−17.2[d]
t-BuO⁻ + acetone	10.8 ± 1.5	0.50 ± 0.07	− 4.5[d]

[a] Standard deviations.

[b] Efficiency = $k_f/k_{Langevin}$ except for the reaction with acetone where efficiency = k_f/k_{ADO}. Values of $k_{Langevin}$ and k_{ADO} were calculated as described in [10].

[c] Estimated (see text).

[d] Taken from [3].

RRKM Calculations. – RRKM equations and general procedures used in the k_2/k_{-1} (see *Figure*) calculations have been discussed in detail elsewhere [4] [5]. Vibrational state sums were calculated using a direct-count procedure for seven frequency groups, and rotations were treated classically.

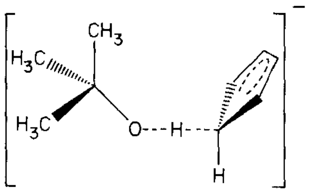
Input parameters for the *t*-butoxide + cyclopentadiene calculations appear in *Table 2*. Frequencies and moments of inertia of cyclopentadiene are known [10] [11]; those for *t*-butoxide were based on *t*-BuOH, *t*-BuF and isobutane [12] [13]. The term I_A/I_B in *Table 2* was used in a correction to the internal energy of transition state B as dictated by angular-momentum conservation [4]. I_A was evaluated by treating the fragments as point masses separated by the *Langevin* capture-radius [14].

Table 2. *Data for* t-*BuO*$^-$ + C_5H_6 *RRKM calculations*[a])

	Transition State A	Transition State B		Transition State A	Transition State B
ν_i	2983 (15)	2975 (14)	I_i, σ_i	38.4,3 (1)	75.8,3 (1)
	1540 (4)	1540 (4)		107.0,1 (2)	40.7,1 (1)
	1398 (11)	1398 (11)		60.0,1 (2)	
	1157 (6)	1168 (8)			
	955 (11)	955 (11)	I_A/I_B	3.11	
	720 (6)	731 (8)			
	364 (10)	364 (10)	σ_B/σ_A	2	

[a]) Degeneracies are in parentheses. Frequencies (ν_i) are in cm^{-1}, moments of inertia (I_i) are in amu Å^2, and σ_i is the symmetry number for the internal rotor. σ_A, σ_B are statistical factors.

Transition state B was assumed to have the geometry **1**.



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The results for the RRKM calculation for *t*-BuO$^-$ + cyclopentadiene are given in *Table 3*.

Table 3. *Results of RRKM calculations for* t-*BuO*$^-$ + C_5H_6[a])

$-\Delta E_H$	6.0	7.0	8.0	9.0	10.0	11.0
Efficiency	0.06	0.15	0.30	0.48	0.65	0.80

[a]) ΔE_H is in kcal mol^{-1} and is the difference $E_0'-E_0$ for the proton transfer reaction. Efficiencies are for the proton transfer reaction.

Discussion. – Ion-molecule collision rates are influenced greatly by the dipole moment and the polarizability of the neutral reactant. Therefore, the results obtained above will be discussed in terms of reaction efficiency (defined as the fraction of collisions which results in reaction) rather than absolute rates. There are different trends among the reaction efficiencies in *Table 1* which will be discussed separately. To a first approximation, *i.e.* assuming similar polarizabilities, well-depths and overall $\Delta H°$'s, the potential surfaces (*Figure*) for the reactions of *t*-butoxide with 2,4-hexadiene and 1,3-cycloheptadiene should differ only entropically. On going to the central transition state, the loss of entropy for the open chain diene will be greater than that for the cyclic one, owing to loss of rotation in the conjugated ion. Experimentally, we indeed observe that the open-chain compound reacts with lower efficiency.

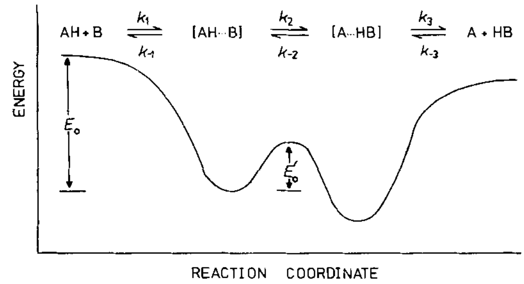
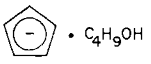


Figure. *Typical energy profile for proton transfer*

Aromaticity of the product anion results in a more exothermic reaction and distinguishes cyclopentadiene from 1,3-cycloheptadiene. It is likely that an enhanced stability of the final product will tend to lower the central-barrier height, and the greater efficiency for cyclopentadiene can be attributed in part to this effect.

Despite a much smaller exothermicity, the reaction efficiency for proton abstraction from acetone is nearly equal to that for cyclopentadiene. Based on entropy considerations (see above), the reaction with acetone should be slower. However, there are major differences between the potential surfaces for the two reactions, arising from differences in the well-depths corresponding to formation of the product and reactant complexes *(Figure)*.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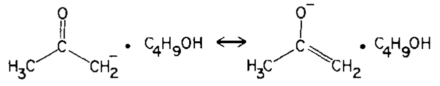
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Let us make an initial (rigorously incorrect, see below) assumption that the reactant-complex well-depths are identical for these two reactions. While product complex **2** is stabilized largely by polarization, **3** may derive additional stabilization from H-bonding to the enolate O-atom. If the central-barrier height is sensitive to the energy difference $\Delta E_{\text{complex}}$ between the product and reactant complexes, this second well-depth may affect the barrier height even more than expected based on the overall reaction exothermicity (since $\Delta E_{\text{complex}}$ can be more negative than ΔH^0) and can explain the increased efficiency for the acetone reaction. An alternative interpretation of the comparable efficiencies despite very different exothermicities involves a larger reactant well-depth with acetone due to its large dipole. Assuming constant barriers (E'_0, *see Fig.*), a larger well-depth (E_0) implies a larger ΔE and consequently a larger reaction efficiency. Thus, increased stability of the reactants' or the products'-complex may compensate for the smaller exothermicity in the reaction of *t*-butoxide with acetone.

Provided the well-depth corresponding to the reactants-encounter complex (E_0) is known, RRKM calculations allow us to obtain an indication of the height of the central-barrier. For the reaction of *t*-butoxide with cyclopentadiene, we obtain from *Table 3* that $E_0 - E'_0 \sim 9$ kcal mol^{-1}. This value is fairly insensitive to changes in the input parameters. The well-depth for *t*-BuO$^-$ + cyclopentadiene is not known; the only data available regarding anion-cyclopentadiene complexes is that of *Kebarle* [15] who studied the thermodynamics of the Cl$^-$-cyclopentadiene cluster and observed that it is 15 kcal mol^{-1} less stable than the Cl^--phenol cluster. The enthalpy of dissociation for the latter is known [16] to be 27.4 kcal mol^{-1}. Assuming the clustering enthalpy to be roughly independent of anion structure, we can estimate a well-depth of 12–13 kcal mol^{-1} for our reaction. Taking this value, we obtain a barrier-height of 3–4 kcal mol^{-1}. Applying *Marcus's* formalism [17], one obtains an intrinsic barrier of 10 kcal mol^{-1} for *t*-BuO^- + cyclopentadiene, which is comparable to intrinsic barriers for proton transfers involving CH acids and bases in solution (*e. g.*, 10 kcal mol^{-1} for protonation of aromatics, and 8 kcal mol^{-1} for deprotonation of carbonyl compounds [18]). Thus, our results provide another piece of evidence for a possible direct correlation between gas-phase and solution-phase intrinsic barriers to proton-transfer reactions [4].

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