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Gas-Phase Acidities and Heats of Formation of 2,4- and 2,5-Cyclohexadien-1-one, the Keto Tautomers of Phenol

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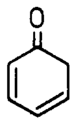
Abstract: The gas-phase acidities and heats of formation of 2,4- and 2,5-cyclohexadien-1-one (**1** and **2**), the keto tautomers of phenol, have been measured by the flowing afterglow technique. The dienones were generated via pyrolytic [4 + 2] cycloreversion reactions of appropriate precursors. Bracketing experiments, involving reactions of **1** and **2** with a series of bases, established that $\Delta H^\circ_{\mathrm{acid}\ 298}(\mathbf{1}) = 344 \pm 3$ kcal mol^{-1} and $\Delta H^\circ_{\mathrm{acid}\ 298}(\mathbf{2}) = 340 \pm 2$ kcal mol^{-1}. $\Delta H^\circ_{\mathrm{f}\ 298}(\mathbf{1}) = -17 \pm 3$ kcal mol^{-1} and $\Delta H^\circ_{\mathrm{f}\ 298}(\mathbf{2}) = -13 \pm 3$ kcal mol^{-1} were assigned by using the known acidity and heat of formation of phenol. The experiments establish unambiguously that the linearly conjugated dienone is more stable than its cross-conjugated isomer. Detailed comparison is made with the previously reported enthalpies of formation and aromatization of 1-methylene-2,4-cyclohexadiene and 1-methylene-2,5-cyclohexadiene (**5** and **6**), the triene tautomers of toluene. The tautomerizations of **1** and **2** to phenol are much less exothermic than the isomerizations of **5** and **6** to toluene, because the former processes entail endothermic enolization of a ketone. Phenol is significantly destabilized relative to toluene (ca. 11–13 kcal mol^{-1}) by enolization. The resonance energies of **2** and **6** and of phenol and toluene are shown to be approximately equal.

Interest in the structure, stability, and reactivity of enols and cyclohexadienones, the tautomers of simple carbonyl compounds and phenols, has stimulated extensive studies of keto–enol tautomerism.[1] Although conjugating or bulky substituents confer remarkable stability upon certain enols and cyclohexadienones,[2] direct observation of these species is normally complicated by their propensity to undergo rapid, exothermic tautomerization. This difficulty notwithstanding, the thermodynamically disfavored enols of several simple carbonyl compounds have been efficiently generated in solution, affording considerable knowledge of their chemistry.[3] A few simple enols have also been studied in the gas phase.[4]

In contrast, little is known about the keto tautomers of phenol, 2,4- and 2,5-cyclohexadienone (**1** and **2**, respectively).[5-8] The parent cyclohexadienones were generated previously by flash vacuum pyrolysis,[9] and infrared and ultraviolet data for **1** and **2** were obtained after immobilization of the pyrolysates at −196 °C. However, efforts to obtain NMR spectra or trap the elusive dienones chemically were thwarted by rapid tautomerization.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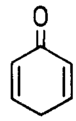
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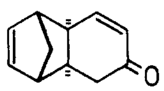
We have generated **1** and **2** in the gas phase and have determined their acidities and heats of formation by using the flowing afterglow technique.[10-12] The cyclohexadienones were prepared via [4 + 2] cycloreversion reactions[13] of **3** and **4**, formal Diels–Alder adducts of **1** and **2** with cyclopentadiene.[14,15] The pyrolyses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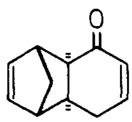
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[1] For a review, see: Toullec, J. *Adv. Phys. Org. Chem.* **1982**, *18*, 1–77.

[2] For leading references, see: (a) Stable enols: Nugiel, D. A.; Rappoport, Z. *J. Am. Chem. Soc.* **1985**, *107*, 3669–3676. (b) Stable cyclohexadienones: Lidert, Z.; McCague, R.; Moody, C. J.; Rees, C. W. *J. Chem. Soc., Perkin Trans. 1* **1985**, 383–389.

[3] For a summary, see: Hart, H. *Chem. Rev.* **1979**, *79*, 515–528. Selected more recent reports: Capon, B.; Siddhanta, A. K.; Zucco, C. *J. Org. Chem.* **1985**, *50*, 3580–3584. Chiang, Y.; Kresge, A. J.; Tang, Y. S.; Wirz, J. *J. Am. Chem. Soc.* **1984**, *106*, 460–462. Capon, B.; Zucco, C. *Ibid.* **1982**, *104*, 7567–7572. Capon, B.; Siddhanta, A. K. *Tetrahedron Lett.* **1982**, *23*, 3199–3203. Ripoll, J.-L. *Nouv. J. Chim.* **1979**, *3*, 195–198. See also: Baigrie, L. M.; Cox, R. A.; Slebocka-Tilk, H.; Tencer, M.; Tidwell, T. T. *J. Am. Chem. Soc.* **1985**, *107*, 3640–3645.

[4] (a) Ethenol and prop-1-en-2-ol: Holmes, J. L.; Lossing, F. P. *J. Am. Chem. Soc.* **1982**, *104*, 2648–2649, and references cited therein. (b) (*E*)- and (*Z*)-prop-1-en-1-ol: Tureček, F. *J. Chem. Soc., Chem. Commun.* **1984**, 1374–1375.

[5] Geminally disubstituted cyclohexadienones, which cannot undergo keto–enol tautomerism, have been widely studied. For reviews, see: (a) Schaffner, K.; Demuth, M. In *Rearrangements in Ground and Excited States*; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 3, pp 281–348. (b) Turro, N. J. *Modern Molecular Photochemistry*; Benjamin/Cummings: Menlo Park, CA, 1978; pp 512–516. (c) Schuster, D. I. *Acc. Chem. Res.* **1978**, *11*, 65–73. (d) Miller, B. *Ibid.* **1975**, *8*, 245–256. (e) Perkins, M. J.; Ward, P. *Mech. Mol. Migr.* **1971**, *4*, 55–112.

[6] The Fe(CO)$_3$ complex of **1** is readily available: Birch, A. J.; Chamberlain, K. B. *Org. Synth.* **1977**, *57*, 107–112, and references cited therein. Fe(CO)$_3$ complexes of simple enols have also been prepared: DePuy, C. H.; Jones, T.; Parton, R. L. *J. Am. Chem. Soc.* **1974**, *96*, 5602–5604, and references cited therein.

[7] (a) Several investigations have implicated transient cyclohexadienones as intermediates in solution (ref 7b) and gas-phase (ref 7c) reactions. (b) See, for example: Takamuku, S.; Matsumoto, H.; Hori, A.; Sakurai, H. *J. Am. Chem. Soc.* **1980**, *102*, 1441–1443, and references cited therein. (c) Jenneskens, L. W.; de Wolf, W. H.; Bickelhaupt, F. *Tetrahedron* **1985**, *41*, 3779–3784.

[8] The 4-bromo derivative of **2** was recently detected in the bromination of phenol: Tee, O. S.; Iyengar, N. R. *J. Am. Chem. Soc.* **1985**, *107*, 455–459, and references cited therein. These investigators estimated that **2** is 15 kcal mol^{-1} higher in enthalpy than phenol at pH 0. For related studies of nitro-substituted dienones, see: Cross, G. G.; Fischer, A.; Henderson, G. N. *Can. J. Chem.* **1984**, *62*, 2803–2812, and references cited therein.

[9] Lasne, M.-C.; Ripoll, J.-L. *Tetrahedron Lett.* **1980**, *21*, 463–464. These authors also prepared 6-methyl-2,4-cyclohexadien-1-one and 4-hydroxy-2,5-cyclohexadien-1-one.

[10] For reviews of flowing afterglow studies of organic anions and description of the experimental technique, see: DePuy, C. H.; Grabowski, J. J.; Bierbaum, V. M. *Science (Washington, DC)* **1982**, *218*, 955–960. DePuy, C. H.; Bierbaum, V. M. *Acc. Chem. Res.* **1981**, *14*, 146–153, and references cited therein.

[11] For a review of gas-phase acidities, see: Bartmess, J. E.; McIver, R. T., Jr. In *Gas Phase Ion Chemistry*; Bowers, M. T., Ed.; Academic Press: New York, 1979; Vol. 2, Chapter 11.

[12] Tautomeric radical cations derived from phenol and **1** have been studied in the gas phase: van Velzen, P. N. T.; van der Hart, W. J.; van der Greef, J.; Nibbering, N. M. M.; Gross, M. L. *J. Am. Chem. Soc.* **1982**, *104*, 1208–1212, and references cited therein. Intensive investigations of gaseous keto–enol radical cation tautomers have been described; for leading references, see: Biali, S. E.; Depke, G.; Rappoport, Z.; Schwarz, H. *J. Am. Chem. Soc.* **1984**, *106*, 496–501.

[13] [4 + 2] Cycloreversions (retro Diels–Alder reactions) were recently reviewed: Lasne, M.-C.; Ripoll, J.-L. *Synthesis* **1985**, 121–143.

[14] Enone **3** was prepared by Diels–Alder reaction of norbornadiene and 1-methoxy-3-((trimethylsilyl)oxy)-1,3-butadiene (Danishefsky's diene), followed by exposure of the adduct to a catalytic amount of trimethylsilyl triflate in tetrahydrofuran. Use of TMSOTf to promote conversion of Diels–Alder adducts of Danishefsky's diene to enones will be the subject of a forthcoming report. **4** was generated by: (i) Diels–Alder reaction of norbornadiene with 1-((trimethylsilyl)oxy)-1,3-butadiene; (ii) desilylation with 0.1 M HCl in tetrahydrofuran; and (iii) oxidation with pyridinium chlorochromate (PCC). Experimental details and spectral data are provided as supplementary material. The cycloaddition reaction conditions were not optimized. For discussion of Diels–Alder reactions of norbornadiene, see: Rondan, N. G.; Paddon-Row, M. N.; Caramella, P.; Mareda, J.; Mueller, P. H.; Houk, K. N. *J. Am. Chem. Soc.* **1982**, *104*, 4974–4976, and references cited therein.

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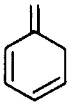
were effected by entrainment of each precursor in a stream of helium at 0.4 torr and passage through a quartz tube heated resistively to ca. 200 °C.[16] The pyrolysates were then swept directly into the flowing afterglow. Under these conditions, the gas-phase acidities of **1** and **2** could be measured by bracketing experiments, involving exposure of each dienone to a series of bases.[17] Dienone **1** was deprotonated by NCO^- (proton affinity (PA) = 344.7 ± 2 kcal mol^{-1}),[18] and by m-$CH_3C_6H_4O^-$ (PA = 350.2 ± 2 kcal mol^{-1}),[19] affording phenoxide ion ($C_6H_5O^-$, m/z 93). However, **1** did not react with p-$ClC_6H_4O^-$ (PA = 343.9 ± 2 kcal mol^{-1})[19] or NO_2^- (PA = 339.8 ± 0.8 kcal mol^{-1}).[20] We therefore assign $\Delta H°_{acid\ 298}(\mathbf{1})$ = 344 ± 3 kcal mol^{-1}.[21,22] Similarly, **2** was deprotonated by NCO^-, p-$ClC_6H_4O^-$, and NO_2^- but not by m-$CF_3C_6H_4O^-$ (PA = 340.2 ± 2 kcal mol^{-1})[19] or weaker bases, so we assign $\Delta H°_{acid\ 298}(\mathbf{2})$ = 340 ± 2 kcal mol^{-1}.[23,24] Possible admixture of the cyclohexadienones with phenol would not interfere with the $\Delta H°_{acid}$ determinations, since phenol is less acidic than either **1** or **2** [$\Delta H°_{acid\ 298}$(phenol) = 349.8 ± 2.6 kcal mol^{-1}].[19] We have not determined whether **1** and **2** partially tautomerize to phenol in the flow tube.

Because deprotonations of **1**, **2**, and phenol afford a common anion, the heats of formation of **1** and **2** can readily be derived from the known heat of formation for phenol (−23.04 ± 0.21 kcal mol^{-1})[25] and the $\Delta H°_{acid}$ data using relation 1.[11]

$$\Delta H°_{f\ 298}(\text{dienone}) - \Delta H°_{f\ 298}(\text{phenol}) = \Delta H°_{acid\ 298}(\text{phenol}) - \Delta H°_{acid\ 298}(\text{dienone}) \quad (1)$$

Thus, $\Delta H°_{f\ 298}$ for **1** and **2** are −17 ± 3 and −13 ± 3 kcal mol^{-i}, respectively, ca. 6 and 10 kcal mol^{-1} greater than the heat of formation of phenol. The uncertainties in the $\Delta H°_{acid}$ and $\Delta H°_f$ values for **1** and **2**, originating primarily in the determinations of the absolute acidities of the reference compounds (e.g., ±2.6 kcal mol^{-1} for phenol), are large in relation to the differences in the acidities and enthalpies of formation of the isomers. Nevertheless, the experiments establish unambiguously that **1** is less acidic and more stable than **2**. The $\Delta H°_f$ data for **1** and **2** apparently comprise the first quantitative measure of the relative stabilities of linearly conjugated and cross-conjugated dienones.[26]

Important conclusions emerge from comparison of our results with those of Bartmess, who determined the gas-phase acidities and heats of formation of the exo-methylene tautomers of toluene (the relatively stable trienes **5** and **6**) by ion cyclotron resonance spectrometry.[27] These analogues of **1** and **2** are both 23 ± 3 kcal mol^{-1} higher in energy than toluene. Thus, tautomerization of **5** or **6** to toluene is much more exothermic than the conversion of **1** or **2** to phenol.



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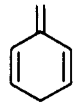

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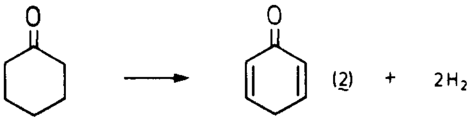
These striking differences in enthalpies of aromatization do not reflect dissimilar resonance energies of the nonaromatic tautomers. We calculated $\Delta H°$ values for formation of **2** and **6** from the nonconjugated species, cyclohexanone and methylenecyclohexane (eq 2 and 3, respectively).[28] The calculations reveal that these processes are equally endothermic, within experimental error [$\Delta H°$ (eq 2) = 41 kcal mol^{-1}, $\Delta H°$ (eq 3) = 43 kcal mol^{-1}]. Hence,



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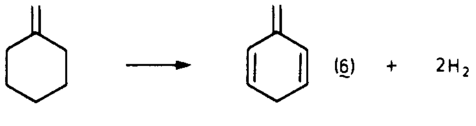

(3)

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(15) Precursor **4** was employed previously in generation of **2** by flash vacuum pyrolysis (ref 9). The published preparation of **1** involved an alternative [4 + 2] cycloreversion.

(16) For a detailed description of the pyrolyzer, see: Damrauer, R.; DePuy, C. H.; Davidson, I. M. T.; Hughes, K. *Organometallics*, in press.

(17) (a) NCO^- and NO_2^- were generated by electron impact on *tert*-butyl isocyanate and N_2O_4, respectively. Formation of the phenoxide bases by deprotonation of the corresponding phenols was precluded by the propensity of the latter to form clusters with anions. However, the phenoxides could be generated by reaction of the respective trimethylsilyl ethers with F^- (ref 17b), produced by electron impact on NF_3. The silyl ethers were prepared by treatment of the phenols with hexamethyldisilazane and a catalytic amount of imidazole (ref 17c). The relatively nonvolatile silyl ethers were introduced by entrainment with ca. one half of the helium buffer gas flow. (b) Cf. Squires, R. R.; DePuy, C. H. *Org. Mass. Spectrom.* **1982**, *17*, 187–191. (c) Cf. Glass, R. S. *J. Organomet. Chem.* **1973**, *61*, 83–90.

(18) Wight, C. A.; Beauchamp, J. L. *J. Phys. Chem.* **1980**, *84*, 2503–2506.

(19) The gas-phase acidities of the substituted phenols were measured relative to phenol: Fujio, M.; McIver, R. T., Jr.; Taft, R. W. *J. Am. Chem. Soc.* **1981**, *103*, 4017–4029. $\Delta H°_{acid\ 298}$(phenol) was reported previously: Cumming, J. B.; Kebarle, P. *Can. J. Chem.* **1978**, *56*, 1–9.

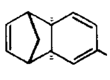
(20) (a) In view of the large uncertainty in the literature value of $\Delta H°_{acid\ 298}$(HONO) (338.3 ± 8 kcal mol^{-1}; ref 11), we derived this quantity by using the relation $\Delta H°_{acid\ 298}(HONO) = \Delta H°_{f\ 298}(H^+) + \Delta H°_{f\ 298}(NO_2^-) - \Delta H°_{f\ 298}(HONO)$, where $\Delta H°_{f\ 298}(NO_2^-) = \Delta H°_{f\ 298}(NO_2) + \Delta H°_{f\ 298}(e^-) - EA(NO_2)$. In this calculation the following values were employed (kcal mol^{-1}): $\Delta H°_{f\ 298}(H^+) = 367.19 \pm 0.01$ (ref 20b); $\Delta H°_{f\ 298}(HONO) = -18.59 \pm 0.45$ (average of values for cis and trans) (ref 20b); $\Delta H°_{f\ 298}(NO_2) = 7.91 \pm 0.2$ (ref 20b); $\Delta H°_{f\ 298}(e^-) = -1.48$ (ref 20c); $EA(NO_2) = 52.46 \pm 0.58$ (ref 20d). (b) Stull, D. R.; Prophet, H. *JANAF Thermochemical Tables*, *NSRDS-NBS-37*, 2nd ed; National Bureau of Standards, Washington, DC, 1971. (c) Cf. Oakes, J. M.; Jones, M. E.; Bierbaum, V. M.; Ellison, G. B. *J. Phys. Chem.* **1983**, *87*, 4810–4815. (d) Woo, S. B.; Helmy, E. M.; Mauk, P. H.; Paszek, A. P. *Phys. Rev.* **1981**, *A24*, 1380–1390.

(21) Proton transfers observed in flowing afterglow studies can be endothermic by 1–2 kcal mol^{-1}; the uncertainties in our $\Delta H°_{acid}$ values are not corrected for this possibility. This ambiguity might be removed by investigating the efficiencies of proton transfer reactions of **1** and **2**, but we cannot measure rates because the pressures of the cyclohexadienones are unknown. For discussion, see: Meot-Ner, M. *J. Am. Chem. Soc.* **1982**, *104*, 5–10.

(22) Reactive neutral molecules (i.e., **1**, **2**, or phenol) could be generated with modest vibrational excitation in our experiments, either in the pyrolyses or, for phenol, via subsequent thermal tautomerizations of the dienones. We estimate that hot neutrals would experience ca. 10^6–10^7 collisions with helium per collision with an anionic reactant. Although the rates of relaxation are not known in detail, we believe that nearly all of the hot neutrals which might be formed would undergo collisional relaxation faster than deprotonation. The immeasurably low pressures of neutral reactants in our experiments, together with the observation of relatively fast proton transfers, indicate that the actual phenoxide precursors must be deprotonated efficiently. Thus we conclude that hot neutrals could give rise to at most a small fraction of the phenoxide ion we detect.

(23) The occurrence of proton transfer from **2** to NO_2^- but not to m-$CF_3C_6H_4O^-$ is accommodated by the uncertainties in the PA's of these ions.

(24) In preliminary deprotonation studies, phenoxide was generated via nonpyrolytic reactions of precursors **3** and **4** with hydroxide ion (PA = 390.8 kcal mol^{-1}: Bartmess, J. E.; Scott, J. A.; McIver, R. T., Jr. *J. Am. Chem. Soc.* **1979**, *101*, 6046–6056). Novel fragmentation reactions of enolates i and ii, or the analogous concerted eliminations, presumably furnished phenoxide and cyclopentadiene. **3** and **4** are not deprotonated by the weaker bases employed in the bracketing experiments, however.



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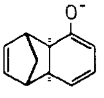

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(25) Cox, J. D.; Pilcher, G. *Thermochemistry of Organic & Organometallic Compounds*; Academic Press: New York, 1970; pp 208–209.

(26) Qualitatively similar enthalpy differences have been calculated for linearly conjugated and cross-conjugated trienes; see, for example: Banks, A.; Mains, G. J.; Bock, C. W.; Trachtman, M.; George, P. *J. Mol. Struct.* **1979**, *56*, 267–275. Note however that the heats of formation of trienes **5** and **6** were previously found to be equal within experimental error (ref 27).

(27) Bartmess, J. E. *J. Am. Chem. Soc.* **1982**, *104*, 335–337.

(28) (a) The experimental heats of formation of **2** (−13 ± 3 kcal mol^{-1}) and **6** (35 ± 3 kcal mol^{-1}; ref 27) were employed in these calculations, together with the literature value for the heat of formation of cyclohexanone (−54.04 ± 0.52 kcal mol^{-1}; ref 25, pp 208–209). The gas-phase heat of formation of methylenecyclohexane is unknown. We derived an estimated value of −8.37 ± 0.34 kcal mol^{-1} from the experimental liquid-phase heat of formation (−17.43 ± 0.20; ref 28b) and the heat of vaporization of the isomeric 1-methylcyclohexene (9.06 ± 0.05; ref 25, pp 152–155), assuming that the heat of vaporization of methylenecyclohexane will be nearly identical. (b) Wiberg, K. B.; Wasserman, D. J.; Martin, E. J.; Murcko, M. A. *J. Am. Chem. Soc.* **1985**, *107*, 6019–6022.

the resonance energies of **2** and **6** are nearly identical.

The tautomerization of **2** is less exothermic than aromatization of **6**, because the former process entails enolization of a ketone. Enolization of cyclohexanone is substantially endothermic ($\Delta H°_{298}$ = 10 kcal mol^{-1}),[29] whereas the analogous isomerization of methylenecyclohexane to 1-methylcyclohexene, related to the aromatization of **6**, imposes no energetic penalty ($\Delta H°_{298} = -2$ kcal mol^{-1}).[30,31] Indeed, $\Delta\Delta H°$ for these simple transformations (12 kcal mol^{-1}) is equal to $\Delta\Delta H°$ for the aromatizations of **2** and **6** (13 kcal mol^{-1}), within experimental error. Comparisons of the heats of formation of both nonaromatic (**2** and **6**) and nonconjugated (cyclohexanone and methylenecyclohexane) structures with those of phenol and toluene[32] thus establish that phenol is significantly destabilized relative to toluene (ca. 11–13 kcal mol^{-1})[33] by enolization. As required by these results, the calculated enthalpies for conversion of cyclohexanone enol to phenol and conversion of 1-methylcyclohexene to toluene likewise differ only slightly ($\Delta H°_{298}$ = 21 and 22 kcal mol^{-1}, respectively).[34] The resonance energies of phenol and toluene are approximately equal.

The success of these ambient temperature flowing afterglow experiments suggests that it may be feasible to study **1** and **2** in solution under carefully controlled conditions.

Acknowledgment. We are grateful to Professor Charles H. DePuy for providing generous access to the flowing afterglow apparatus and to Dr. Veronica M. Bierbaum for helpful discussions. The flowing afterglow studies were supported by the National Science Foundation (Grant CHE-8503505).

Registry No. 1, 24599-57-3; **2**, 5664-33-5; **3**, 103201-40-7; **4**, 103301-79-7; PhOH, 108-95-2.

Supplementary Material Available: Synthetic protocols and spectral data for **3** and **4** (2 pages). Ordering information is given on any current masthead page.

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[29] The heat of formation of the enol of cyclohexanone was calculated (−43.7 kcal mol^{-1}) by using the group additivity method: Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; Wiley: New York, 1976. The group value for O-(C$_d$)(H) proposed by Holmes and Lossing (−44.6 kcal mol^{-1}; ref 4a) was employed. For the heat of formation of cyclohexanone, see footnote 28.

[30] The heat of formation of 1-methylcyclohexene is −10.34 ± 0.20 kcal mol^{-1} (ref 25, pp 152–153). For estimation of the heat of formation of methylenecyclohexane, see footnote 28.

[31] A similar argument involving **1** and **5** likewise suggests that enolization is primarily responsible for the smaller exothermicity of the aromatization of **1**, compared with tautomerization of **5**.

[32] $\Delta H°_{f\,298}$(toluene) = 11.99 ± 0.10 kcal mol^{-1} (ref 25, pp 152–153).

[33] $\Delta\Delta H°$ for (cyclohexanone $\rightarrow$ phenol + $2H_2$) and (methylenecyclohexane $\rightarrow$ toluene + 2 H_2) is 11 kcal mol^{-1}.

[34] By using heats of formation given above, enthalpies of reaction were calculated for (cyclohexanone enol $\rightarrow$ phenol + $2H_2$) and (1-methylcyclohexene $\rightarrow$ toluene + $2H_2$).

Product-Determining Steps in Gas-Phase Brønsted Acid–Base Reactions. Deprotonation of 1-Methylcyclopentyl Cation by Amine Bases

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Abstract: Experimental results are presented for deprotonation of 1-methylcyclopentyl cation (**1**) by ammonia, trimethylamine, and 1-methylcyclopentylamine at pressures below 10^{-3} Torr, which yields two neutral products, 1-methylcyclopentene (**2**) and methylenecyclopentane (**3**). The isomer ratio varies from **2**:**3** = 2.74 for ammonia to 1.34 for trimethylamine, consistent with previous reports. FTMS measurement of ion–molecule reaction rates of **1** plus ammonia gives an efficiency of 0.34 when **1** is generated by a 20–70 eV electron impact on bromocyclohexane. Reaction of the perdeuterated cation **1**-d_{11} with ammonia yields products that reveal only a very low level of hydrogen scrambling between acid and base. Isotope effects on the reaction rate and the neutral product ratio, determined from experiments using **1**-d_{11} or ND_3, are found to be small. Two mechanistic alternatives are discussed: Lewis (in which covalent acid–base complexes are formed) and Eigen (in which hydrogen-bonded intermediates are formed). Reaction of **1**-d_{11} with 1-methylcyclopentylamine shows only a small amount of interchange of deuterated and undeuterated alkyl groups, which argues against a Lewis mechanism as an obligatory pathway. Experimental results are interpreted in terms of orbiting intermediates, in which acidic C–H bonds and the basic nitrogen experience large deviations from collinearity. More than one subsequent step is required for the reactants to engage chemically. In order for Eigen mechanisms to operate, a C–H bond must point toward the nitrogen, which requires loss of some internal degrees of freedom. For proton transfer to be completed, the nitrogen lone pair must be pointed along the C—H···N axis, which requires loss of additional degrees of freedom. Progress of the reaction beyond the initially formed orbiting intermediate is described by a scheme in which these stages of approach to reactive orientation represent discrete steps.

When a Brønsted acid transfers a proton to a base, the reaction passes through several transition states. In solution, participation of solvent molecules plays an important role, and it may happen that no single step is rate-determining. In the gas phase, the absence of solvent reduces the complexity of the molecular interactions, but the intervention of at least one intermediate, as represented by reaction 1, demands that there be at least two transition states.[1] Several years ago we reported distributions of isomeric olefins from deprotonation of tertiary alkyl cations that possess chemically nonequivalent acidic hydrogens.[2] Using a specially constructed Electron Bombardment Flow (EBFlow) reactor for collecting the neutral products of ion–molecule reactions, we observed that the thermodynamically less stable olefins were recovered in high proportions, sometimes exceeding the yield of their more stable isomers. We pointed out that this could not be explained in terms of a single intermediate that decomposes

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[1] Chesnavich, W. J.; Su, T.; Bowers, M. T. *J. Am. Chem. Soc.* **1978**, *100*, 4362–4367.

[2] Marinelli, W. J.; Morton, T. H. *J. Am. Chem. Soc.* **1978**, *100*, 3536–3539; **1979**, *101*, 1908.

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