Electron Affinities from Thermal Proton-Transfer Reactions: C_6H_5 and $C_6H_5CH_2$

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Received June 4, 1971

The observation of the preferred direction of proton transfer reactions in the gas phase at 300 °K has been employed to bracket the electron affinity, e.a., of the radicals C_6H_5 and $C_6H_5CH_2$ using well-established values for electron affinities and bond energies. The results indicate that $1.2\ \mathrm{eV} \leq$ e.a.$(C_6H_5) \leq 1.6\ \mathrm{eV}$ and that $0.4\ \mathrm{eV} \leq$ e.a.$(C_6H_5CH_2) \leq 0.9\ \mathrm{eV}$.

Les observations relatives à la direction préférentielle dans les réactions de transfert de proton en phase gazeuse et à 300 °K, ont été utilisées pour encadrer la valeur e.a. d'électron affinité pour les radicaux C_6H_5 et $C_6H_5CH_2$; à cet effet, des valeurs d'électron affinité et d'énergie de liaison bien établies, ont été utilisées. Les résultats indiquent que $1.2\ \mathrm{eV} \leq$ e.a.$(C_6H_5) \leq 1.6\ \mathrm{eV}$ et que $0.4\ \mathrm{eV} \leq$ e.a.$(C_6H_5CH_2) \leq 0.9\ \mathrm{eV}$.

Canadian Journal of Chemistry, 49, 2918 (1971)

Chemically useful values for the electron affinity of small molecules have recently become accessible through gas-phase investigations of the kinetics of negative ion – molecule reactions. For example, exothermic and endothermic negative-ion charge-transfer reactions have been employed to bracket unknown electron affinities between well-established electron affinities (1, 2). Electron affinities of molecules have also been determined from the translational energy thresholds for endothermic charge transfer reactions involving atomic halogen anions (3).

We report here the determination of electron affinities of selected radicals from bracketing experiments involving proton transfer reactions of the type

$$[1] \qquad X^- + YH \leftrightarrows Y^- + XH$$

proceeding in the gas phase at 300 °K. Although bracketing experiments can surpass the precision of other earlier techniques, they lack the precision of photodetachment (4) and electron impact (5) methods which, however, are often limited to the study of the electron affinity of atoms and small molecules.

The determination of the preferred direction of proton transfer in reaction 1 identifies the sign of the standard free energy change which, in turn, identifies the sign of the standard enthalpy change if the change in standard entropy can be neglected. The standard enthalpy change, ΔH°, for reaction 1, is related to bond dissociation energy, D, and electron affinity, e.a., parameters in the following manner

$$[2] \quad \Delta H^\circ = D(\mathrm{YH}) - D(\mathrm{XH}) + \mathrm{e.a.}(\mathrm{X}) - \mathrm{e.a.}(\mathrm{Y})$$

Thus a knowledge of the sign of ΔH° and three of the four energy parameters allows the determination of a limiting value for the fourth parameter. The parameter of interest in these studies was the electron affinity of either X or Y.

The experiments were performed in a flowing afterglow system at the National Oceanic and Atmospheric Administration, Environmental Research Laboratories, in Boulder, Colorado. Details of the method of operation and data analysis have been thoroughly described elsewhere (6, 7). Helium was used as the buffer gas at a pressure *ca.* 0.4 Torr. H^- ions were generated by 25 eV electron impact on NH_3. The production of OH^- and $C_3H_5^-$ has been described previously (7) as has the generation of $C_6H_5^-$ and $C_6H_5CH_2^-$ (8). The concen-

Table 1. Summary of the kinetics of proton-transfer reactions investigated in the gas phase at 300 °K

Proton-transfer reaction	k_f*	k_r*	K
$C_6H_5^- + H_2O \rightleftarrows OH^- + C_6H_6$	$\gtrsim 5(-11)$	$< 5(-12)$	> 10
$H^- + C_6H_6 \rightleftarrows C_6H_5^- + H_2$	$\gtrsim 5(-11)$	$< 5(-12)$	> 10
$C_6H_5CH_2^- + C_2H_5OH \rightleftarrows C_2H_5O^- + C_6H_5CH_3$	$\gtrsim 5(-11)$	$< 5(-11)$	> 1
$C_3H_5^- + C_6H_5CH_3 \rightleftarrows C_6H_5CH_2^- + C_3H_6$	$\sim 1(-11)$	$< 1(-12)$	> 10
$OH^- + C_3H_6 \rightleftarrows C_3H_5^- + H_2O$	$2.7(-10)$		

*Units in cm^3 $molecule^{-1}$ s^{-1}, (-11) denotes 10^{-11}.

trations of water, benzene, ethanol, and toluene in the reaction region were measured by monitoring the increase in total pressure in the reaction region as the vapors were introduced. As a result of the insensitivity of the capacitance manometer (with a 10 Torr sensing head) used in these experiments, the rate determinations for fast reactions using this technique led only to limiting values for rate constants.

A summary of the rate constant data obtained is given in Table 1. The last reaction listed has been reported previously (7). The ratio of the forward to the reverse rate constant was taken to be equal to the thermodynamic equilibrium constant since the energy distribution of both the ions, which undergo many thousand collisions with helium atoms before entering the reaction region, and the neutral reactants, which are added in thermal equilibrium at the operating temperature, is expected to be Boltzmann in all the forward and reverse reactions investigated. For each of the reactions listed in Table 1, the thermodynamic equilibrium constant was found to be greater than 1. Hence the standard free energy change is negative for all these reactions as written. We now make the assumption that the transfer of a proton is not accompanied by a significant change in entropy, *i.e.*, $T\Delta S° \ll \Delta H°$. Consequently, the five reactions listed in Table 1 are taken to be exothermic or thermoneutral at 300 °K. Relation 2 then leads to the limiting values $1.2\ eV \leq e.a.(C_6H_5) \leq 1.6\ eV$ and $0.4\ eV \leq e.a.(C_6H_5CH_2) \leq 0.9\ eV$. The electron affinities of H, OH, and C_2H_5O are taken to be well established at 0.754 eV (9), 1.83 eV (10), and 1.68 eV (11), respectively. The bond energies for H—H, HO—H, C_2H_5O—H, C_6H_5—H, and $C_6H_5CH_2$—H were taken to be 4.477 (12), 5.11 (12), 4.43 (13), 4.86 (14), and 3.69 (13), respectively.

The authors are aware of only one previous experimental determination of the electron affinity of these radicals. Page and Goode, who employ the magnetron technique they developed (15), report values ranging from 2.15 to 2.46 eV for e.a.(C_6H_5) and values ranging from 0.76 to 0.84 eV (with one value of 2.5 eV) for e.a.($C_6H_5CH_2$). An early molecular orbital theory calculation by Hush and Pople (16) yielded e.a.($C_6H_5CH_2$) = 0.69 eV. The limiting values for e.a.($C_6H_5CH_2$) determined in these studies are in good agreement with the values (0.76 to 0.84 eV) determined by the magnetron technique and the value obtained from theoretical calculations. However, the limiting values determined in this study suggest a value for e.a.(C_6H_5) considerably lower than that obtained from the magnetron technique. An electron affinity e.a.(C_6H_5) > 2.0 eV would make the first reaction in Table 1 endothermic (and $\Delta G° > 0$) for ground-state reactants at 300 °K by more than 0.3 eV. We expect that our kinetic measurements deal with ground-state $C_6H_5^-$ ions and not $C_6H_5^-$ excited. Hence our result should represent a more accurate value for the electron affinity of C_6H_5.

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