inclusion of vibrational zero-point energies. Our results, of course, refer only to the gas-phase process, and the experimentally observed rearrangement can (and probably does) proceed by a significantly different path.

**Acknowledgment.** This work was supported by the Robert A. Welch Foundation, through Grant Y-743.

**Registry No.** $CNBH_3^-$, 35798-27-7; $NCBH_3^-$, 33195-00-5; $CNB(CH_3)_3^-$, 79735-17-4; $NCB(CH_3)_3^-$, 44248-05-7; $CNBCl_3^-$, 79735-18-5; $NCBCl_3^-$, 79735-19-6; $CNBF_3^-$, 68830-29-5; $NCBF_3^-$, 79735-04-9; $CNAlH_3^-$, 79735-05-0; $NCAlH_3^-$, 79735-06-1; $CNAl(CH_3)_3^-$, 79735-07-2; $NCAl(CH_3)_3^-$, 79735-08-3; $CNAlCl_3^-$, 79735-09-4; $NCAlCl_3^-$, 79735-10-7; $CNAlF_3^-$, 79735-11-8; $NCAlF_3^-$, 79735-12-9; $CNB(CH_3)H_2^-$, 79735-13-0; $CNB(CH_3)_2H^-$, 79735-14-1; $NCB(CH_3)H_2^-$, 79735-15-2; $NCB(CH_3)_2H^-$, 79735-16-3; $BH_3$, 13283-31-3; $B(CH_3)_3$, 593-90-8; $BCl_3$, 10294-34-5; $BF_3$, 7637-07-2; $AlH_3$, 7784-21-6; $Al(CH_3)_3$, 75-24-1; $AlCl_3$, 7446-70-0; $AlF_3$, 7784-18-1.

---

# Carbon–Hydrogen Bond Dissociation Energies in Alkylbenzenes. Proton Affinities of the Radicals and the Absolute Proton Affinity Scale

**Michael Meot-Ner (Mautner)**

*Contribution from the Chemical Thermodynamics Division, National Bureau of Standards, Washington, D.C. 20234. Received April 17, 1981*

**Abstract:** Rate constants ($k$) were measured for proton-transfer reactions from alkylbenzene ions $RH^+$ to a series of reference bases B, i.e., $RH^+ + B \rightarrow BH^+ + R\cdot$. For exothermic reactions ($\Delta H \leq -1$) $k$ is large, but as weaker bases are used and the reaction becomes thermoneutral the collision efficiency decreases sharply. The variation of $k$ with $\Delta H$ determines the proton affinity (PA) of the radical R· relative to a set of reference bases to within ±0.5 kcal mol$^{-1}$. For example, the reaction $C_6H_5CH_3^+ + B \rightarrow BH^+ + C_6H_5CH_2\cdot$ is fast (reaction efficiency = $k/k_{col} \geq 0.5$) when B = MeO-$t$-Bu or stronger bases, but $k/k_{col}$ is significantly smaller when B is $n$-Pr$_2$O or weaker bases. From the falloff curve of reaction efficiency vs. PA(B), we find PA($n$-Pr$_2$O) = PA($C_6H_5CH_2\cdot$) + 0.8 kcal mol$^{-1}$ = 200.0 kcal mol$^{-1}$. Since PA($C_6H_5CH_2\cdot$) is obtained from known thermochemical data, this relation defines the absolute PA of $n$-Pr$_2$O. Through a ladder of known PA, we then obtain PA($i$-$C_4H_8$) = 186.8 kcal mol$^{-1}$; we also obtain the absolute PAs of other oxygen bases. Falloff curves of reaction efficiencies of $3\text{-}FC_6H_4CH_3^+$, $C_6H_5C_2H_5^+$, $C_6H_5$-$n$-$C_3H_7^+$, and $C_6H_5$-$i$-$C_3H_7^+$ with these reference bases give then the following PAs of R· and R–H bond dissociation energies ($D^\circ$) (all in kcal mol$^{-1}$) as R·, PA(R·), $D^\circ$(R–H): $3\text{-}FC_6H_4CH_2\cdot$, 197.2, 89.4; $C_6H_5\dot{C}HCH_3$, 197.9, 86.2; $C_6H_5\dot{C}HC_2H_5$, 199.1, 86.1; $C_6H_5(CH_3)_2$, 199.6, 86.1. In a similar manner, rate constants for $H^+$ transfer from $C_6H_5NH_2^+$ to reference pyridines and amines yield PA($C_6H_5NH\cdot$) = 221.5 and $D^\circ$($C_6H_5NH$–H) = 85.1 kcal mol$^{-1}$ (1 kcal mol$^{-1}$ = 4.18 kJ mol$^{-1}$).

## I. Introduction

It has been assumed for some time that the occurrence or nonoccurrence of proton-transfer reactions such as

$$RH^+ + B \rightarrow BH^+ + R\cdot \qquad (1)$$

can be used to distinguish between exothermic and endothermic processes, respectively. Using this principle, the proton affinity (PA) of R· can be bracketed by two references bases such that PA($B_1$) < PA(R·) < PA($B_2$). This relation can be used for the following: (1) if PA(R·) is known independently, the absolute PAs of $B_1$ and/or $B_2$ can be estimated; or (2) conversely, if PA($B_1$) or PA($B_2$) is known, PA(R·) can be bracketed. In conjunction with ionization potential data (see below), these measurements also yield the bond dissociation energy $D^\circ$(R–H) and the heat of forrmation $\Delta H_f^\circ$ (R·). Recently, DeFrees et al.[1] used this bracketing method to measure the PA and $\Delta H_f^\circ$ of several hydrocarbon radicals including $C_6H_5CH_2\cdot$.

One limitation to the accuracy by which this bracketing technique defines thermochemical values is that the transition from fast kinetics to "nonoccurrence" in a set of reactions is, in fact, gradual, rather than abrupt. While strongly exothermic reactions are usually fast, reactions closer to thermoneutral are usually slower,[2] and, on the other hand, slightly endothermic reactions may still proceed at detectable rates. This fact usually limits the accuracy of the *bracketing* measurements to within ±2 kcal mol$^{-1}$. In the present work we set out to measure rate constants for reactions of $RH^+$ with a set of bases B whose PAs are closely spaced. This way we can better quantify the transition from fast to slow kinetics, and therefore we can define with better accuracy the thermoneutral point in such a set of reactions. This should yield improved accuracy in relating the PAs of alkylbenzene radicals R· to the PAs of the reference bases B.

We shall use this method to: (a) relate the PAs of some reference bases to the absolute PA of $C_6H_5CH_2\cdot$ which in turn can be calculated from available data (thereby we can obtain the absolute PAs of the reference bases), and (b) we will then measure PAs of several other alkylbenzene radicals and calculate from these data R-H bond dissociation energies. We shall show that differences as small as 0.5 kcal mol$^{-1}$ between the PAs of alkylbenzene radicals can be clearly measured by this kinetic technique.

## II. Experimental Section

The measurements were performed on the NBS pulsed ion cyclotron resonance (ICR) mass spectrometer, using standard techniques.[3,4] In most experiments the gases RH and B were admitted in two separate inlets; in a few kinetic experiments and most equilibrium measurements premixed mixtures were used. Every rate constant was measured in at least three different mixtures with different RH:B ratios. These ratios usually ranged from 10:1 to 1:2. Total source pressures were 1 to 4 × $10^{-6}$ Torr.

---

(1) DeFrees, D. G.; McIver, R. T.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 3334.

(2) Lias, S. G.; Shold, D. M.; Ausloos, P. *J. Am. Chem. Soc.* **1980**, *102*, 2540, and ref 5, 8, and 9 therein.

(3) Lias, S. G.; Euler, J. R.; Ausloos, P. *Int. J. Mass Spectrom. Ion Phys.* **1976**, *19*, 219.

(4) Lias, S. G.; Ausloos, P.; Horvath, Z. *Int. J. Chem. Kinet.* **1976**, *8*, 719.

Table I. Rate Constants[a] and Reaction Efficiencies of Proton-Transfer Reactions: $RH^+ + B \rightarrow BH^+ + R\cdot$

| B | $C_6H_5CH_3$ |  | $C_6H_5CD_3$ |  | $3\text{-}FC_6H_4CH_3$ |  | $C_6H_5C_2H_5$ |  | $C_6H_5\text{-}n\text{-}C_3H_7$ |  | $C_6H_5\text{-}i\text{-}C_3H_7$ |  | PA(B) (kcal $mol^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  | $k$ | $k/k_{ADO}$ | $k$ | $k/k_{ADO}$ | $k$ | $k/k_{ADO}$ | $k$ | $k/k_{ADO}$ | $k$ | $k/k_{ADO}$ | $k$ | $k/k_{ADO}$ |  |
| sec-$Bu_2O$ | 8.1 | 0.57 |  |  |  |  | 6.0 | 0.44 | 5.4 | 0.41 | 5.0 | 0.38 | 206.7[c] |
| i-$Pr_2O$ | 6.4 | 0.46 | 5.8 | 0.41 | 6.6 | 0.48 | 4.2 | 0.31 | 5.5 | 0.41 | 4.2 | 0.32 | 203.9[c] |
| n-$Bu_2O$ | 11.6 | 0.82 |  |  |  |  | 7.8 | 0.60 | 7.4 | 0.45 | 3.7 | 0.28 | 201.4[c] |
| MeOtBu | 6.7 | 0.51 | 6.1 | 0.47 | 6.0 | 0.48 | 4.6 | 0.37 | 4.9 | 0.40 | 3.9 | 0.32 | 200.0[c] |
| n-$Pr_2O$ | 4.9 | 0.35 |  |  | 6.6 | 0.48 |  |  | 3.0 | 0.23 | 0.24 | 0.018 | 199.6[c] |
| $Et_2CO$ | 2.3 | 0.13 | 2.7 | 0.15 | 8.4 | 0.49 | 5.4 | 0.32 | 2.4 | 0.14 |  |  | 198.6[d] |
| MeCO-i-Pr | 1.5 | 0.10 | 1.6 | 0.09 | 7.1 | 0.38 | 5.5 | 0.30 | 2.0 | 0.11 |  |  | 198.5[e] |
| MeCOOEt | 0.47 | 0.032 |  |  | 3.8 | 0.26 | 1.6 | 0.12 |  |  |  |  | 198.0[d] |
| $Et_2O$ | 0.27 | 0.021 | ≤0.44 | 0.034 | 3.4 | 0.27 | 1.3 | 0.10 | 0.20 | 0.02 | 0 |  | 197.6[d] |
| EtCOOMe |  |  | 0.51 | 0.067 | 3.0 | 0.21 |  |  |  |  |  |  | 197.4[e] |
| MeCOEt |  |  |  |  | 2.4 | 0.12 | 0.63 | 0.03 |  |  |  |  | 197.1[d] |
| THF | 0 |  | 0 |  | 1.7 | 0.12 |  |  |  |  |  |  | 196.9[e] |
| MeCOOMe |  |  |  |  | 0.3 | 0.02 |  |  |  |  |  |  | 195.5[d] |

[a] In units of $10^{-10}$ $cm^3$ $s^{-1}$. [b] $k_{ADO}$ = collision rate constant calculated from ADO theory (ref 5). [c] From relative gas-phase basicities obtained in this work (Table IV). [d] From relative gas-phase basicities in ref 2. [e] From Taft, R. W., private communication to Lias, S. G.

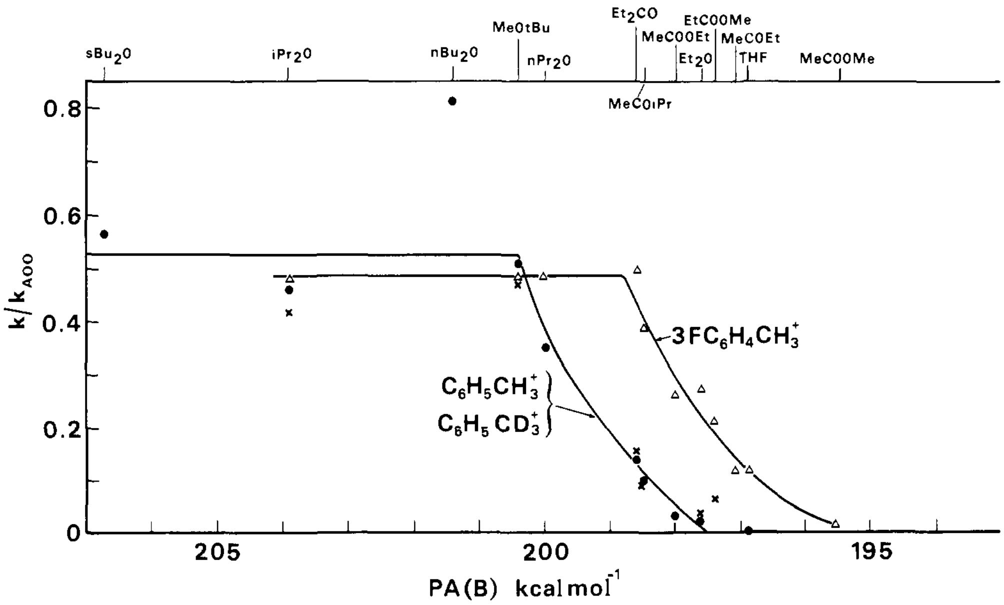

Figure 1. Reaction efficiencies as measured by $k/k_{ADO}$ vs. proton affinities of reference bases, for $RH^+ + B \rightarrow BH^+ + R\cdot$. The reactant ions are indicated on the plot; bases B on upper abscissa.

In order to minimize the internal energy of $RH^+$, the energy of the ionizing electrons was kept as close to IP(RH) as possible, generally below 10 eV. The electron energy was low enough so that all the fragment ion intensities, especially $R^+$, were less than 10% of $RH^+$. This simplified the mass spectrum and also generally avoided ionization of the reference bases B. Nevertheless, we checked the effect of ionization energy on the rate constants for some selected reactions, and we found no effect. For example, $k$ for $C_6H_5CD_3^+$ + MeCO-i-Pr → MeCO-i-$PrD^+$ + $C_6H_5CD_2$ was $1.6 \times 10^{-10}$ at 9.0 eV nominal electron energy, where only the molecular ion of $C_6H_5CD_3^+$ was present, and the same at 24.0 eV where substantial fragmentation of the toluene ion occurs.

The fact that the ionizing electron energy does not affect the rate constant indicates that the ions are not produced with significant internal energies. To check this further, we measured all the rate constants over pressure ranges that varied by factors of up to 2.5. We did not observe any systematic pressure effects. For example, the rate constant for the reaction of $C_6H_5\text{-}n\text{-}C_3H_7^+$ with n-$Pr_2O$ was measured at total pressures of 1.60 and $3.82 \times 10^{-6}$ Torr as 2.9 and 3.1 ± 0.6 $10^{-10}$ $cm^3$ $s^{-1}$, respectively, without systematic variation over the entire pressure range.

Moreover, we always observed the proper exponential decay of the reactant ions throughout the reaction times which were usually followed through 50 to 120 ms after the ionizing pulse. Both the lack of pressure effect and the observation of exponential decay indicate that excess internal energy of $RH^+$ does not play any observable role in the reactions; otherwise, collisional removal of the internal energy from the ions would decrease the rate constant with increasing reaction time or pressure.

All the materials used were of commercial sources with purities of at least 98% and were used without further purification. The mass spectra never indicated any significant impurities. Isomeric impurities cannot be ruled out; however, the presence of up to 5% impurities in the reactants would still not significantly affect the rate constants.

## III. Rate Constants of Proton Transfer from Alkylbenzene Ions to Reference Bases. Effects off $\Delta H°$

The rate constants $k$ and reaction efficiencies $k/k_{ADO}$, where $k_{ADO}$ represents the average dipole orientation (ADO) theory[5] collision rates, for reactions of the type of reaction 1 are summarized in Table I. On the basis of the consistency of replicate measurements in sets of three to four different mixtures, we estimate the accuracy as ±20% for reactions with rate constants $>2 \times 10^{10}$ $cm^3$ $s^{-1}$. For slower reactions the errors may be up to ±40%.

The rate constants were obtained from the rate of disappearance of the reactant ions $RH^+$ in the presence of B. Correction was made for nonreactive ion losses. In all the alkylbenzene ion reactions with bases B the IP of B was higher than that of RH by at least 0.5 eV, so that charge-transfer channels from $RH^+$ to B can be ruled out. Further the fact that the collision efficiencies are controlled in a systematic manner by the proton affinities of B (see Figures 1 and 2) also indicates that channels other than reaction 1 do not contribute significantly to the reactivity between $RH^+$ and B. Nevertheless, for some representative reactions we checked that the appearance of $BH^+$ compensated for the loss of $RH^+$, i.e., that $RH^+$ did not disappear significantly through other channels. The following systems were

---

(5) Su, T.; Bowers, M. T. *Int. J. Mass Spectrom. Ion Phys.* **1975**, *17*, 211.

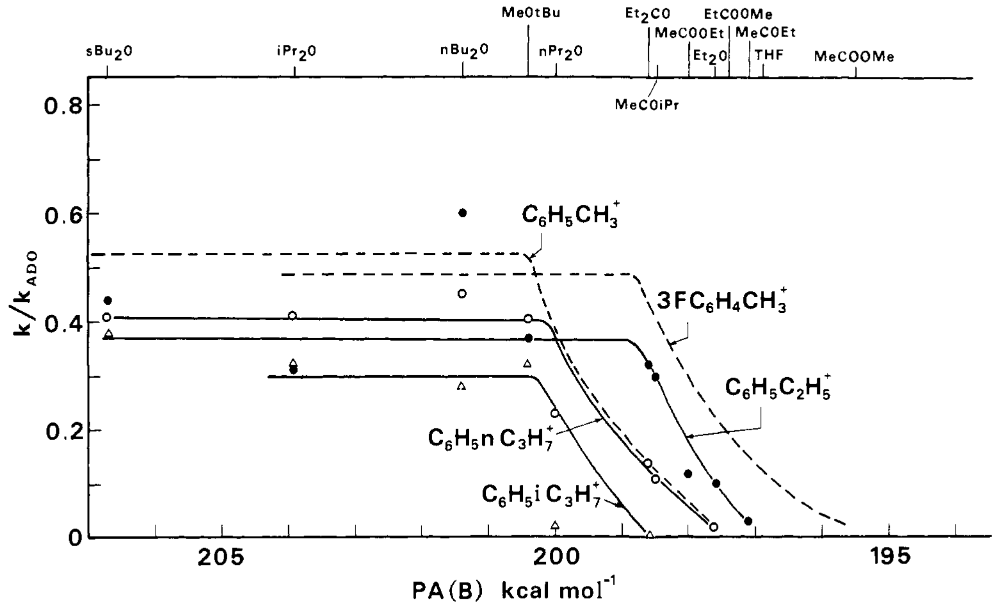

**Figure 2.** Reaction efficiencies as measured by $k/k_{ADO}$ vs. proton affinities of reference bases, for $RH^+ + B \rightarrow BH^+ + R\cdot$. The reactant ions are indicated on the plot; bases on upper abscissa.

checked in this manner (RH, B): $C_6H_5CD_3$, $i$-$Pr_2O$; $C_6H_5CD_3$, $Et_2CO$; $C_6H_5CD_3$, MeCO-$i$-Pr; $C_6H_5$-$n$-$C_3H_7$, $n$-$Pr_2O$; $C_6H_5$-$n$-$C_3H_7$, $Et_2CO$; $C_6H_5$-$i$-$C_3H_7$, $n$-$Pr_2O$; $C_6H_5$-$t$-$C_4H_9$, $i$-$Pr_2O$; $C_6H_5NH_2$, 2,4-dimethylpyridine; $C_6H_5NH_2$, 4-methylpyridine; $C_6H_5NH_2$, $Me_3N$. For several of the reactions we checked by double resonance ejection of $RH^+$ that $BH^+$ was indeed produced by reaction 1. The following reaction systems were checked in this manner (RH, B): $C_6H_5C_2H_5$, EtCOMe; $C_6H_5$-$n$-$C_3H_7$, $n$-$Pr_2O$; $C_6H_5$-$i$-$C_3H_7$, $n$-$Bu_2O$; $C_6H_5$-$i$-$C_3H_7$, $i$-$Pr_2O$; $C_6H_5CD_3$, $Et_2O$; $C_6H_5CD_3$, MeCO-$i$-Pr; $C_6H_5CD_3$, $Et_2O$; $C_6H_5$-$n$-$C_3H_7$, $Et_2CO$.

The collision efficiencies of the reactions of $C_6H_5CH_3^+$ with a series of reference bases B are plotted in Figure 1 as a function of the relative proton affinities (PA) of B. Efficiencies for reactions of $C_6H_5C_2H_5^+$, $C_6H_5C_3H_7^+$ and $C_6H_5$-$i$-$C_3H_7^+$ with bases B are similarly plotted in Figure 2. We shall comment below on the PA scale used in Figures 1 and 2. Each plot in Figures 1 and 2 reaches at sufficiently high exothermicities a limiting high efficiency which then remains approximately constant with further increase in PA(B). The rate constant falls off over a range of about 2–3 kcal $mol^{-1}$ in the PA(B) when we get to sufficiently weak bases. We associate this transition from fast to slow kinetics with the transition from exothermic to endothermic reactions, respectively. In rough approximation the reaction efficiency is $\approx 0.5$ at the point where the reaction is thermoneutral, since then the proton will be attached with equal probability to either reactant when the reaction complex dissociates. In fact, Lias et al.[2] observed that proton transfer from $t$-$C_4H_9^+$ to oxygen bases slows to about 30% of its fast kinetic limit at the point when the reaction is thermoneutral. We shall consider the proton affinity of each R· to be defined by the point on the abscissa where the reaction efficiency falls to 0.5 of its fast reaction limit. Beyond this point further decrease in $k/k_{ADO}$ occurs owing to endothermicity; e.g., at 320 K an activation energy of 1 kcal $mol^{-1}$ decreases $k$ by a factor of 5. Since the falloff curves of $k/k_{ADO}$ vs. PA(B) are steep, our procedure defines the PA of R· within $\pm 0.5$ kcal $mol^+$. We must note that the presence of significant vibrational energy in the $RH^+$ ions woud decrease the accuracy as it would make the endothermic reactions faster and thus affect the falloff curves. For reasons stated above we do not feel that this is a significant source of error under our conditions.

## IV. Steric Effects on Rate Constants

Inspecting the kinetic data, we observe that the "fast-reaction" limit for the present reactions is apparently affected by steric effects. It is evident from Table I and Figure 1 that the fast-reaction limit for all reactants is significantly below unit efficiency, i.e., $k/k_{ADO} \leq 0.6$. Moreover, the limiting efficiencies decrease with increasing steric crowding of the reactive proton in $RH^+$, i.e., in the order $C_6H_5CH_3^+ \approx$ 3-$FC_6H_4CH_3^+ > C_6H_5C_2H_5 \approx C_6H_5$-$n$-$C_3H_7^+ > C_6H_5$-$i$-$C_3H_7^+$. For example, this order of efficiencies is observed in the reactions of the various $RH^+$ ions with the strongest base $sec$-$Bu_2O$ (see Table I, row I). The steric hindrance of the bases also seems to play a role: in general, the reaction efficiencies of a given $RH^+$ with $i$-$Pr_2O$ and $sec$-$Bu_2O$ are lower than with $n$-$Bu_2O$, although the former reactions are more exothermic. Evidently proton transfer to $i$-$Pr_2O$ and $sec$-$Bu_2O$ is slowed down because of steric hindrance of the proton acceptor site by the branched substituents. When both $RH^+$ and B are sterically hindered as in the reactions of $C_6H_5$-$i$-$C_3H_7^+$ with $i$-$Pr_2O$ and $sec$-$Bu_2O$, the combined steric hindrances reduce the reaction efficiency to about 0.3. Similar effects of steric hindrance on proton transfer reactions were observed in alkylpyridines.[6]

## V. The Reactions of $C_6H_5CH_3^+$ and $C_6H_5CD_3^+$

Rate constants and collision efficiencies for the reactions of $C_6H_5CH_3^+$ and $C_6H_5CD_3^+$ ions are shown in Table i and Figure 1. We consider that these reactions reach their fast limit at MeO-$t$-Bu, at the collision efficiency of 0.50. According to the falloff curves of Figure 1, the reactions reach half of the maximum efficiency at a point which is lower by 0.8 kcal $mol^{-1}$ on the PA scale than $n$-$Pr_2O$. We consider this as the thermoneutral point; therefore

$$PA(n\text{-}Pr_2O) = PA(C_6H_5CH_2\cdot) + 0.8 \text{ kcal mol}^{-1} \quad (2)$$

In the next section we shall use this relation to define the absolute PA scale of the reference bases.

Figure 1 shows that the falloff curves of $C_6H_5CH_3^+$ and $C_6H_5CD_3^+$ overlap. However, because of the zero-point-energy difference the C–D bond should be stronger by about 1 kcal $mol^{-1}$ than the C–H bond. Since the IP's of the two molecules are equal to within 0.1 kcal $mol^{-1}$, the $D^+$ affinity of $C_6H_5CD_2\cdot$ ought to be higher than the $H^+$ affinity of $C_6H_5CH_2\cdot$ (see eq 4 below). Therefore, the curve of $C_6H_5CD_3^+$ ought to be shifted to the left by ca. 1 kcal $mol^{-1}$ in Figure 1. The fact that the two curves overlap indicates that the O-$D^+$ bonds formed in the bases are also stronger than the O-$H^+$ bonds, and the overall thermochemistry of proton transfer reactions is equal to that of the deuteron-transfer reactions.

The bracketing reactions of DeFrees et al. place the PA of $C_6H_5CH_2\cdot$ between THF and the MeOAc, while our more detailed

---

(6) Jasinski, J. M.; Brauman, J. I. *J. Am. Chem. Soc.* **1980**, *102*, 2906.

measurements place it between $Et_2CO$ and $i\text{-}Pr_2O$. According to our results the PA of $C_6H_5CH_2\cdot$ is therefore higher by 3 kcal $mol^{-1}$ than the value given by DeFrees et al.

While DeFrees et al.[1] report reaction between $C_6H_5CH_3^+$ and tetrahydrofuran (THF), we found that no reaction takes place. Because of this discrepancy we investigated the $C_6H_5CD_3$– THF system in some detail. In a mixture of $2.1 \times 10^{-6}$ Torr of $C_6H_5CD_3$ and $2.1 \times 10^{-6}$ Torr of THF, at 14-eV electron energy, we observed no significant decay of the $C_6H_5CD_3^+$ ion. However, $THFH^+$ was forrmed, presumably by fast reaction between $THF^+$ formed by electron impact and THF. The $THFH^+$ ion intensity did not change when $C_6H_5CD_3^+$ was ejected by double resonance. The $THFH^+$ ion intensity decreased with reaction time, possibly mostly because of the formation of $THFH^+\cdot THF$ dimer. During this time $THFD^+$ formation was also observed, and this ion also did not respond to double resonance ejection of $C_6H_5CD_3^+$ which showed that it was not formed from the $C_6H_5CD_3^+$ ion. These observations suggest that $THFD^+$ was formed by the isotope exchange reaction:

$$THFH^+ + C_6H_5CD_3 \rightarrow THFD^+ + C_6H_5CH_2D \tag{3}$$

and we found $k = 4 \times 10^{-10}$ $cm^3$ $s^{-1}$ for this reaction. These conclusions as to the origin of $THFH^+$ and $THFD^+$ were also supported by the fact that at 9.5-eV electron energy where $C_6H_5CD_3^+$ is ionized but THF is not, neither $THFH^+$ nor $THFD^+$ is observed. While $C_6H_5CD_3^+$ does not react with THF, the complex chemistry of the system under the conditions used by DeFrees et al.[1] may erroneously suggest the occurrence of this reaction.

### VI. Proton Affinity of $C_6H_5CH_2\cdot$ and the Absolute Proton Affinity Scale

As we noted in the Introduction, the PAs of the radicals R·, the R–H bond dissociation energies, and the IPs of RH are related to each other by thermochemical relations. These relationships result from the cycle in eq 4. Now $\Delta H°_{I}$ = IP(RH), $\Delta H°_{II}$ =

$$\begin{tikzcd}
RH \arrow[r, "1"] \arrow[d, "III"'] & RH^+ + e \arrow[d, "II"] \\
R\cdot + H \arrow[r, "IV"] & R\cdot + H^+ + e
\end{tikzcd} \tag{4}$$

PA(R·), $\Delta H°_{III}$ = $D°$(R–H), and $\Delta H°_{IV}$ = IP(H·). Using these relations we derive:

$$D°(R\text{–}H) = IP(RH) + PA(R\cdot) - IP(H\cdot) \tag{5}$$

We can calculate the PA of $C_6H_5CH_2\cdot$ since the other necessary quantities in eq 5 are known. We use the values of IP($C_6H_5CH_3$) = 203.4 ± 1.1 and IP(H·) = 313.7 kcal $mol^{-1}$ as recommended by Rosenstock et al.[7] and $D°(C_6H_5CH_2\text{-}H)$ = 88.9 kcal $mol^{-1}$ as given recently by Tsang.[8] Equation 5 then yields PA($C_6H_5CH_2\cdot$) = 199.2 kcal $mol^{-1}$.

According to relation 2 as obtained from the rate-constant falloff curve, we therefore find PA($n\text{-}Pr_2O$) = 200.0 kcal $mol^{-1}$. Using the scale of gas-phase basicities of ref 2 at 320 K and neglecting entropy corrections (see below), we calculate the absolute PA of $CH_3COCH_3$ as 194.5 kcal $mol^{-1}$ and of $i\text{-}C_4H_8$ as 193.0 kcal $mol^{-1}$. We use $\Delta H_f°(i\text{-}C_4H_8) = -4.3$ kcal $mol^{-1}$.[23] We obtain from eq 6 $\Delta H_f°(t\text{-}C_4H_9^+)$ = 168.5 kcal $mol^{-1}$. This derivation of PA($i\text{-}C_4H_8$) and $\Delta H_f°(t\text{-}C_4H_9^+)$ from the kinetic results involves the use of several approximations, the use of PA reference data, and IP values which require comment.

$$\Delta H_f°(t\text{-}C_4H_9^+) = \Delta H_f°(H^+) + \Delta H_f°(i\text{-}C_4H_8) - PA(i\text{-}C_4H_8) \tag{6}$$

**a. Basicities and Proton Affinities of Reference Bases.** Several scales of relative gas-phase basicities of our reference compounds have been reported. The values relevant to the present work were summarized by Lias et al.,[2] who obtained one of these scales in this laboratory.[2,9-12] The three scales reviewed by Lias et al.[2] agree as to the value of interest here, which is the difference [PA($n\text{-}Pr_2O$) – PA($i\text{-}C_4H_8$)] = 7.0 ± 0.3 kcal $mol^{-1}$.

Some proton affinities were obtained from proton-transfer equilibria in the present work (Table IV).

**b. Relation between Basicities and Proton Affinities.** To calculate relative enthalpies of protonation (PAs) from gas-phase basicities (i.e., $\Delta G°_{320}$, of proton transfer) entropy changes are often considered to be accounted for by changes in rotational symmetry that are assumed to take place upon protonation. For example, $\sigma_{rot}$ of $CH_3COCH_3$ is expected to change from 2 to 1 upon protonation. However, Ausloos and Lias[13] and also Yamdagni and Kebarle[11] found experimentally that $\Delta S°_{320} = 0.0 \pm 0.3$ cal $mol^{-1}$ for

$$CH_3COCH_3\cdot H^+ + i\text{-}C_4H_8 \rightleftarrows t\text{-}C_4H_9^+ + CH_3COCH_3 \tag{7}$$

and also that $\Delta S°$ is negligible individually for the protonation of $CH_3COCH_3$ and $i\text{-}C_4H_8$ as well as of $C_3H_6$ (propene). These results suggest that for molecules with free rotors such as $CH_3COCH_3$ only a small fraction of the thermal population is in the highest symmetry conformation, while conformations with lower symmetry are predominant. Therefore, the change of the molecular rotational symmetry number from 2 to 1 upon the protonation of symmetric molecules such as $CH_3COCH_3$, $C_2H_5OC_2H_5$, etc., may not be applicable. Also, the corrections due to $\sigma_{rot}$ effects are within the magnitude of the experimental error for the present data. Therefore, we shall neglect these corrections, and we equate relative GB's with relative PA's for all the present compounds. The uncertainty in using $\Delta S° = 0 \pm 1$ cal $mol^{-1}$ $K^{-1}$ introduces an uncertainty of ±0.3 kcal $mol^{-1}$ in the PA values derived in this manner.

**c. Ionization Energies.** Equation 4 requires the use of IP(RH) to calculate PA(R·). We shall use the adiabatic 0 K values given in the literature, which are close to the 300 K values for alkylbenzenes of low symmetry.[14] Also, we shall use the stationary electron convention; i.e., we shall not take into account the thermal energy of the electron at 300 K. This does not affect the absolute PA values and $D°$(R–H) values obtained from eq 5 where only differences between IPs occur, but it does affect the ionic heats of formation derived from relations such as eq 6,8, and 9.

Our result of $\Delta H_f°_{298}(t\text{-}C_4H_9^+)$ = 168.5 kcal $mol^{-1}$ may be compared with several recent values from the literature. Several studies derive this value from the IP of $t\text{-}C_4H_9\cdot$ (eq 8). In order to compare these values with the present result in a consistent manner, we shall use in eq 8 all the conventions and approximations detailed above, i.e., IP(0 K) = IP(300 K), k.E.($e^-$) = 0, and $D°(t\text{-}C_4H_9\text{-}H)$ = 96.6 kcal $mol^{-1}$.

$$\Delta H_f°_{300}(t\text{-}C_4H_9^+) = \Delta H_f°_{300}(t\text{-}C_4H_9\cdot) + IP(t\text{-}C_4H_9\cdot) \tag{8}$$

$$\Delta H_f°_{300}(t\text{-}C_4H_9^+) = \Delta H_f°_{300}(i\text{-}C_4H_{10}) + D°(t\text{-}C_4H_9\text{-}H) - \Delta H_f°(H) + IP(t\text{-}C_4H_9\cdot) \tag{9}$$

Using IP($t\text{-}C_4H_9\cdot$) = 154.5 kcal $mol^{-1}$, as obtained by Houle and Beauchamp,[15] gives $\Delta H_f°_{300}(t\text{-}C_4H_9^+)$ = 166.6 kcal $mol^{-1}$. This value is in reasonable agreement with that of Traeger and McLoughlin,[16] who obtain $\Delta H_f°_{300}(i\text{-}C_4H_9^+) \leq 166.2 \pm 0.8$ kcal $mol^{-1}$. Both of these values are lower by more than 2 kcal $mol^{-1}$ than our result. However, Traeger and McLoughlin[16] also obtain

---

(7) Rosenstock, H. M.; Draxl, K.; Steiner, B. W.; Herron, J. T. *J. Phys. Chem. ref. data* **1977**, *6*, Suppl. No. 7.

(8) Tsang, W. In "Shock Tubes in Chemical Technology"; A. Lipschitz, Ed.; Marcel Dekker: New York, in press. We use this value as it is the most recent and currently recommended value by Tsang.

(9) Wolf, J. F.; Staley, R. H.; Koppel, I.; Taagepera, M.; McIver, R. T.; Beauchamp, J. L.; Taft, R. W. *J. Am. Chem. Soc.* **1977**, *99*, 5417.

(10) Aue, D. H.; Bowers, M. T. In "Gas Phase Ion Chemistry", M. T. Bowers, Ed.; Academic Press: New York, 1979.

(11) Yamdagni, R.; Kebarle, P. *J. Am. Chem. Soc.* **1976**, *98*, 1320.

(12) Lau, Y. K. Ph.D Thesis, University of Alberta, 1979.

(13) Ausloos, P.; Lias, S. G. *J. Am. Chem. Soc.* **1978**, *100*, 1953.

(14) Lias, S. G.; Ausloos, P. *J. Am. Chem. Soc.* **1978**, *100*, 6027.

(15) Houle, F. A.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1979**, *101*, 4067.

(16) Traeger, J. C.; McLoughlin, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 3647.

Table II. Thermochemical Values Related to the Alkylbenzene Radicals R·: Bond Dissociation Energies of R-H and Proton Affinities of R·[a]

| radical R- | IP(RH) | $\Delta H_f{}^\circ{}_{298}$-(RH)[b] | PA(R·) | $D^\circ{}_{298}$-(R-H) | $\Delta H_f{}^\circ{}_{298}$-(R·) |
|---|---|---|---|---|---|
| $C_6H_5CH_2\cdot$ | 203.4[c] | 12.0 | 199.2 | (88.9) | 48.8 |
| $3\text{-}FC_6H_4CH_2\cdot$ | 205.6[c] | | 197.2 | 89.4 | |
| $C_6H_5\underset{\cdot}{C}HCH_3$ | 202.0[c] | 7.2 | 197.9 | 86.2 | 41.3 |
| $C_6H_5\underset{\cdot}{C}HCH_2CH_3$ | 200.7[d] | 1.9 | 199.1 | 86.1 | 35.9 |
| $C_6H_5\dot{C}(CH_3)_2$ | 200.2[d] | 1.0 | 199.6 | 86.1 | 35.0 |
| $C_6H_5NH\cdot$ | 177.3[d] | 20.8 | 221.5 | 85.1 | 54.7 |

[a] All units in kcal mol$^{-1}$. [b] From ref 19. [c] From ref 7. [d] From equilibrium measurements, related to IP: $C_6H_5CH_2CH_3$ = 202.6 kcal mol$^{-1}$ as reference (see Table IV). [e] From ref 8.

$\Delta H_f{}^\circ{}_{300}(i\text{-}C_3H_7{}^+)$ = 191.8 ± 0.4 kcal mol$^{-1}$; this can be combined with the result of Lias et al.,[2] i.e., $\Delta H_f{}^\circ{}_{300}(i\text{-}C_3H_7{}^+) - \Delta H_f{}^\circ{}_{300}(t\text{-}C_4H_9{}^+)$ = 22.4 kcal mol$^{-1}$ to yield $\Delta H_f{}^\circ(t\text{-}C_4H_9{}^+)$ = 169.4 kcal mol$^{-1}$, which is in good agreement with the present value of 168.5 kcal mol$^{-1}$. Moreover, the values for $\Delta H_f{}^\circ{}_{300}(i\text{-}C_3H_7{}^+)$ = 190.8[17] and 192.5 kcal mol$^{-1}$ [18] can also be combined with the result of Lias et al.[2] to give $\Delta H_f{}^\circ(t\text{-}C_4H_9{}^+)$ = 168.4 and 170.1 kcal mol$^{-1}$, which differ only by −0.1 and +1.6 kcal mol$^{-1}$, respectively, from the present result. Also, the value of IP($i\text{-}C_3H_7\cdot$) = 169.7 kcal mol$^{-1}$ by Houle and Beauchamp,[15] combined with $D^\circ$-($(CH_3)_2CH\text{-}H$) = 97.3 kcal mol$^{-1}$, gives $\Delta H_f{}^\circ{}_{300}(i\text{-}C_3H_7{}^+)$ = 190.1 kcal mol$^{-1}$, from which we obtain $\Delta H_f{}^\circ(t\text{-}C_4H_9{}^+)$ = 167.7 kcal mol$^{-1}$. Finally, the average of $\Delta H_f{}^\circ(i\text{-}C_3H_7{}^+)$ = 191.3 kcal mol$^{-1}$ using the values from ref 15–18, combined with the result of Lias et al.[2], leads to $\Delta H_f{}^\circ{}_{300}(t\text{-}C_4H_9{}^+)$ = 168.9 kcal mol$^{-1}$, in excellent agreement with the present result.

## VII. Proton Affinities of Alkylbenzene Radicals R·. R-H Bond Dissociation Energies

The falloff curves of reaction efficiencies in Figures 1 and 2 can be used along the lines we followed above, to find the PAs of the radicals $3\text{-}FC_6H_4CH_2\cdot$, $C_6H_5\dot{C}HCH_3$, $C_6H_5\dot{C}HCH_2CH_3$, and $C_6H_5\dot{C}(CH_3)_2$, in relation to the absolute PA scale as defined in the previous section. We then obtain the PA values listed in Table II.

First we observe that relative PAs that differ by as little as 0.4 kcal mol$^{-1}$ are quite clearly distinguishable by the kinetic technique, as is observed in the difference between the falloff curves of $3\text{-}FC_6H_5CH_3{}^+$ and $C_6H_5C_2H_5{}^+$ (Figure 2). Indeed, if the curves of $C_6H_5CH_3$ and $C_6H_5\text{-}n\text{-}C_3H_7$ are compared (Figure 2), it appears that even the difference of only 0.3 kcal mol$^{-1}$ between the corresponding radical PAs may be meaningful.

According to eq 5, the PAs of the radicals depend on two physical factors: they increase as IP(RH) decreases, and increase as $D^\circ$(R–H) increases. Table II provides two pairs of radicals where the effect of IP(RH) on PA(R·) can be observed directly. Going from toluene to 3-fluorotoluene the IP(RH) increases by 2.2 kcal mol$^{-1}$ which causes an approximately equal decrease by 1.7 kcal mol$^{-1}$ in PA(R·). Likewise, going from $C_6H_5C_2H_5$ to $C_6H_5\text{-}n\text{-}C_3H_7$, IP(RH) decreases by 1.3 kcal mol$^{-1}$, leading to an increase by 1.2 kcal mol$^{-1}$ in PA(R·). In considering these results it should be kept in mind that the relative IPs of these compounds were measured by charge-transfer equilibria (Table IV), while the relative PAs were determined independently from the kinetic falloff curves. The agreement between variations of IP(R–H) and PA(R·) to the level of a few tenths of a kcal mol$^{-1}$ therefore indicates the level of accuracy of both kinds of measurements.

The R–H bond dissociation energies in Table II mostly follow expected trends. The primary benzyl C–H bond in toluene is not expected to be affected by the 3-F substitution. The secondary C–H bonds of $C_6H_5CH\text{-}HCH_3$ and $C_6H_5CH\text{-}HCH_2CH_3$ are also expected to be equal. Both statements are confirmed by the data. $D^\circ$(R–H) for the secondary C–H bonds is expected to be lower than the primary benzyl C–H bonds. The difference of 2.7 kcal mol$^{-1}$ is comparable to the difference of 3.5 kcal mol$^{-1}$ between the $D^\circ$ of $CH_3CH_2\text{-}H$ and $(CH_3)_2CH\text{-}H$.[8]

Table III. Rate Constants and Reaction Efficiencies for $C_6H_5NH_2{}^+ + B \rightarrow C_6H_5NH\cdot + BH^+$

| B | $k$[a] | $k/k_{ADO}$ | PA(B)[b] |
|---|---|---|---|
| isopropylamine | ⩽0.17 | ⩽0.01 | 216.5 |
| *n*-hexylamine | 0.43 | 0.03 | 217.2 |
| *tert*-amylamine | 1.60 | 0.12 | 219.4 |
| trimethylamine | 7.0 | 0.62 | 221.4 |
| diethylamine | 10.4 | 0.79 | 222.4 |
| pyridine | ≈0 | ≈0 | 217.5 |
| 3-methylpyridine | 2.7 | 0.15 | 219.9 |
| 4-methylpyridine | 4.6 | 0.26 | 220.8 |
| 2,4-dimethylpyridine | 16.7 | 0.95 | 224.0 |

[a] In units of cm$^3$ s$^{-1}$. [b] In kcal mol$^{-1}$. Relative proton affinities from ref 10, but absolute values adjusted to PA($i\text{-}Pr_2O$) = 200 kcal mol$^{-1}$ as reference.

Table IV. Auxiliary Proton-Transfer and Charge-Transfer Equilibrium Measurements

| | $-\Delta G^\circ$ [a] |
|---|---|
| $n\text{-}Pr_2OH^+ + n\text{-}Bu_2O \rightleftarrows n\text{-}Bu_2OH^+ + n\text{-}Pr_2O$ | 1.4 |
| $n\text{-}Pr_2OH^+ + MeOtBu \rightleftarrows MeO\text{-}t\text{-}BuH^+ + n\text{-}Pr_2O$ | 0.2 |
| $n\text{-}Bu_2OH^+ + i\text{-}Pr_2O \rightleftarrows i\text{-}Pr_2OH^+ + n\text{-}Bu_2O$ | 2.5 |
| $i\text{-}Pr_2OH + t\text{-}Bu_2O \rightleftarrows sec\text{-}Bu_2OH^+ + i\text{-}Pr_2O$ | 2.8 |
| $3\text{-}FC_6H_4CH_3{}^+ + C_6H_5CH_3 \rightleftarrows C_6H_5CH_3{}^+ + 3\text{-}FC_6H_4CH_3$ | 2.6 |
| $C_6H_5C_2H_5{}^+ + C_6H_5\text{-}n\text{-}C_3H_7 \rightleftarrows C_6H_5\text{-}n\text{-}C_3H_7{}^+ + C_6H_5C_2H_5$ | 1.3 |
| $C_6H_5\text{-}n\text{-}C_3H_7{}^+ + C_6H_5\text{-}t\text{-}C_4H_9 \rightleftarrows C_6H_5\text{-}t\text{-}C_4H_9{}^+ + C_6H_5\text{-}n\text{-}C_3H_7$ | 1.3 |
| $C_6H_5\text{-}i\text{-}C_3H_7{}^+ + C_6H_5\text{-}t\text{-}C_4H_9 \rightleftarrows C_6H_5\text{-}t\text{-}C_4H_9{}^+ + C_6H_5\text{-}i\text{-}C_3H_7$ | 0.8 |

[a] In kcal mol$^{-1}$. Error estimated as ±0.2 kcal mol$^{-1}$. All values at 335 K.

One somewhat unexpected result is that $D^\circ$ for the tertiary bond in $C_6H_5C\text{-}H(CH_3)_2$ is equal to the secondary bonds in ethyl and propylbenzene. If an analogy is drawn to the difference between $D^\circ(t\text{-}C_4H_9\text{-}H)$ and $D^\circ(i\text{-}C_3H_7\text{-}H)$, our results agree with the recent tabulation of Tsang[8] which shows that the difference is negligible; however, this is in variance with earlier tabulations, such as by Benson,[21] which suggest that the tertiary bond should be weaker by 2.5 kcal mol$^{-1}$.

In relation to the falloff curve of the reactions of $C_6H_5\text{-}i\text{-}C_3H_7$ in Figure 2, we should comment that the falloff was considered to take place between MeO-*t*-Bu and $Et_2CO$; this gives a slope similar to the other curves. However, the reaction with $n\text{-}Pr_2O$ gives an anomalously low point. If the falloff was taken to occur between MeO-*t*-Bu and $n\text{-}Pr_2O$, $D^\circ$ of the tertiary C–H bond would be about 1 kcal mol$^{-1}$ higher. The steric factors involved in the reaction of $C_6H_5CH(CH_3)_2$ may be responsible for this uncertainty.

## VIII. Reactions of the Aniline Ion: $C_6H_5NH\text{-}H$ Bond Dissociation Energy

We observed in the ICR mass spectrometer that the aniline ion does not react with the parent compound aniline. The reaction of $C_6H_5NH_2{}^+$ with reference bases can be observed, therefore,

---

(17) Baer, T. J. *J. Am. Chem. Soc.* **1980**, *102*, 2482.

(18) Chupka, W. A.; Berkowitz, J. *J. Chem. Phys.* **1967**, *47*, 2921; reevaluated in ref 16.

(19) Stull, D. R.; Westrum, E. G., Jr.; Linke, G. C. "The Chemical Thermodynamics of Organic Compounds"; Wiley: New York, 1969.

(20) Taking $D^\circ(H_2N\text{-}H)$ = 103 kcal mol$^{-1}$ (ref 22) and assuming that $D^\circ(CH_3NH\text{-}H)$ is 6 kcal mol$^{-1}$ lower, i.e., 97 kcal mol$^{-1}$, in analogy with the difference $D^\circ(C_2H_5\text{-}H) - D^\circ(CH_3\text{-}H)$ = 6 kcal mol$^{-1}$ (ref 21).

(21) Benson, S. W. "Thermochemical Kinetics", 2nd ed.; Wiley-Interscience: New York, 1976.

(22) Darwent, B. *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand.* No. 31, 1971.

(23) Cox, J. D., Pitcher, G. "Thermochemistry of Organic and Organometallic Compounds"; Academic Press: New York, 1970.

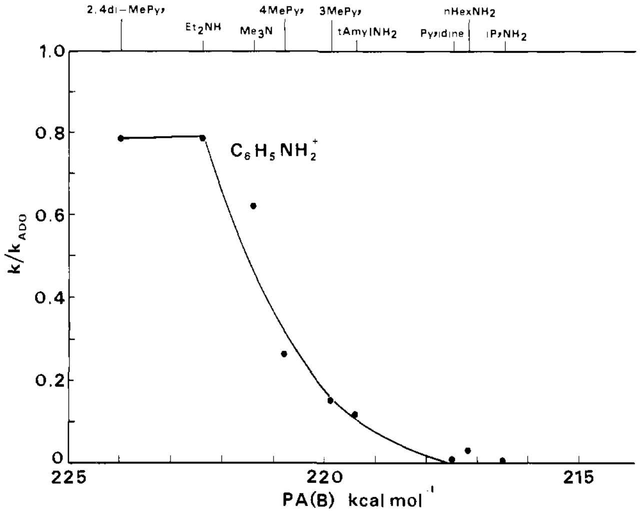

**Figure 3.** Reaction efficiencies as measured by $k/k_{\mathrm{ADO}}$ vs. proton affinities of reference bases, for $RH^+ + B \rightarrow BH^+ + R\cdot$, where $RH^+$ is the aniline ion; bases indicated on upper abscissa.

without complications. Rate constants and reaction efficiencies are given in Table III.

The reaction efficiencies as a function of PA(B) are given in Figure 3. Proton affinities of the reference bases were obtained using relative gas-phase basicities of amines and pyridines by Aue and Bowers.[10] Entropy considerations were handled as above, except that small entropy corrections were made owing to changes in $\sigma_{\mathrm{rot}}$ of the amine group due to protonation. The absolute PA values were related to the PA of $n$-$Pr_2O$ as above.

From the falloff curve of Figure 3 we obtain PA($C_6H_5NH\cdot$) = 221.5 kcal mol$^{-1}$. Equation 5 then gives $D°(C_6H_5NH{-}H)$ = 85.1 kcal mol$^{-1}$. The difference between $D°(CH_3NH{-}H)$[20] and $D°(C_6H_5NH{-}H)$, due to resonance stabilization of the $C_6H_5NH\cdot$ radical, is 12 kcal mol$^{-1}$. This is similar to the resonance stabilization of $C_6H_5CH_2\cdot$, as compared with $CH_3CH_2\cdot$, which is about 14 kcal mol$^{-1}$.[21]

**Acknowledgment.** The author thanks Dr. P. Ausloos for suggesting this problem, and Drs. P. Ausloos and S. G. Lias for their continued interest and many helpful discussions during this work.

**Registry No.** Pyridine, 110-86-1; 3-methylpyridine, 108-99-6; 4-methylpyridine, 108-89-4; 2,4-dimethylpyridine, 108-47-4; *sec*-$Bu_2O$, 6863-58-7; *i*-$Pr_2O$, 108-20-3; *n*-$Bu_2O$, 142-96-1; MeO-*t*-Bu, 1634-04-4; *n*-$Pr_2O$, 111-43-3; $Et_2CO$, 96-22-0; MeCO-*i*-Pr, 563-80-4; MeCOOEt, 141-78-6; $Et_2O$, 60-29-7; EtCOOMe, 554-12-1; MeCOEt, 78-93-3; THF, 109-99-9; MeCOOMe, 79-20-9; $C_6H_5CH_3^+$, 34504-47-7; $C_6H_5CD_3^+$, 38091-11-1; 3-$FC_6H_4CH_3^+$, 58436-59-2; $C_6H_5C_2H_5^+$, 39600-67-4; $C_6H_5C_3H_7^+$, 53649-54-0; $C_6H_5$-*i*-$C_3H_7^+$, 68199-09-7; $C_6H_5CH_2\cdot$, 2154-56-5; 3-$FC_6H_4CH_2\cdot$, 2599-73-7; $C_6H_5\dot{C}HCH_3$, 2348-51-8; $C_6H_5\dot{C}HCH_2CH_3$, 19019-92-2; $C_6H_5\dot{C}(CH_3)_2$, 4794-07-4; $C_6H_5NH\cdot$, 2348-49-4; $C_6H_5CH_3$, 108-88-3; $C_6H_5CD_3$, 1124-18-1; 3-$FC_6H_4CH_3$, 352-70-5; $C_6H_5C_2H_5$, 100-41-4; $C_6H_5$-*n*-$C_3H_7$, 103-65-1; $C_6H_5$-*i*-$C_3H_7$, 98-82-8; $C_6H_5NH_2$, 62-53-3; *i*-$PrNH_2$, 75-31-0; *n*-hex$NH_2$, 111-26-2; *t*-amyl$NH_2$, 594-39-8; $Me_3N$, 75-50-3; $Et_2NH$, 109-89-7; *n*-$Pr_2OH^+$, 17009-84-6; *n*-$Bu_2OH^+$, 17009-85-7; *i*-$Pr_2OH^+$, 17009-86-8; *t*-$Bu_2O$, 6163-66-2; $C_6H_5$-*t*-$C_4H_9$, 98-06-6; $C_6H_5NH_2^+$, 34475-46-2; *t*-$Bu^+$, 14804-25-2.

---

# Electron Spin Echo Studies of Cholestane Nitroxide Motion in Lecithin Multibilayer Dispersions and Vesicles: Detection of Nitroxide Probe Motion and Vesicle Rotation

**Keith Madden,[1] Larry Kevan,*[2] Philip D. Morse II,[3] and Robert N. Schwartz[4]**

*Contribution from the Departments of Chemistry and Biological Sciences, Wayne State University, Detroit, Michigan 48202, Department of Chemistry, University of Houston, Houston, Texas 77004, and Department of Chemistry, University of California, Los Angeles, California 90024. Received May 4, 1981*

**Abstract:** Electron spin echo spectroscopy has been used to *directly* measure the electron spin transverse relaxation time $T_2$ vs. temperature of the 3-doxyl-5$\alpha$-cholestane nitroxide spin probe in egg yolk lecithin vesicles. In a preliminary study of cholestane nitroxide in isotropic liquids and in egg yold lecithin multibilayer dispersions (*J. Phys. Chem.* **1980**, *84*, 2691), the electron spin echo decay function was a single exponential attributed to motion of the spin probe. In contrast, the echo decay in vesicles exhibits fast and slow exponential decay components associated with spin probes with their long axes perpendicular and parallel to the magnetic field. In addition a new fast component appears at high temperatures which is attributed to vesicle rotation which moves a population of slowly relaxing spin probes into an orientation having faster relaxation. This appears to be the first *direct* observation of vesicle rotation by electron magnetic resonance.

The study of molecular motion in organized molecular assemblies such as bilayers, micelles, and vesicles is of considerable importance in understanding their biological and chemical functions. These systems have been extensively studied by incorporating paramagnetic probes and by using continuous wave electron spin resonance (CW ESR) to indirectly deduce the electron spin transverse relaxation time $T_2$ of the probe molecule.[5] $T_2$ is the reciprocal half-width at half-height of a *homogeneously* broadened ESR line and contains information on the motion of the probe. Unfortunately, the ESR resonances of nitroxide spin probes are inhomogeneously broadened by unresolved intramolecular hyperfine interactions[6] and a detailed knowledge of the magnitude of these interactions along with iterative spectral simulation procedures are required to obtain an estimate of $T_2$.[6-8]

---

[1] Radiation Laboratory, University of Notre Dame, Notre Dame, IN 46556.

[2] Wayne State University and University of Houston.

[3] Department of Biological Sciences, Wayne State University.

[4] On leave from the Department of Chemistry, University of Illinois at Chicago Circle, Chicago, IL 60680.

[5] Berliner, L. J. Ed. "Spin Labeling Theory and Applications"; Academic Press: New York, 1976.

[6] Stillman, A. E.; Schwartz, R. M. *J. Magn. Reson.* **1976**, *22*, 269.

0002-7863/82/1504-0010$01.25/0