for the complexing of zinc(II) glycinate with the temperature-jump technique.

A noticeable feature of the present results is that the K_{12} and k_{23} values indicate ligand dependences; i.e., the association constant K_{12} is larger while the rate constant k_{23} is smaller with the higher carboxylate. For the confirmation of the above result, in the first place the experimental data were examined by a method of analysis analogous to that given by Brintzinger and Hammes.²⁰ Rearranging eq 5, we obtain

$$\tau = \frac{K_{12}K_{23}}{k_{23}K_1} \left\{ 1 + \frac{K_{23}}{1 + K_1([\mathbf{M}] + [\mathbf{X}])} \right\}$$
(8)

where τ is the relaxation time with $\tau^{-1} = 2\pi f_r$. The τ vs {1 + $K_1([M] + [X])^{-1}$ plot gave a straight line for each reaction system. The reaction parameters evaluated from the slopes and intercepts of these lines agree with those of Table II. In the second place, the effects of the medium on the reaction parameters should be examined; the high ionic strength adopted in this study might affect the activity coefficients of the systems studied in different ways for the different carboxylate ions to result in the ligand dependences observed. According to the potentiometric studies by Gerding,²¹ the K_1 value of cadmium(II) acetate decreases only 7% by the variation of the ionic strength from 0.25 to 2 M. Thus, the medium effect on the activity coefficient factor of K_{12} 's would be, even if it differed from system to system, of this order of magnitude. As for the rate constant k_{23} , the medium effect should be much less, since the rate constant involves the ratio of the activity coefficients of the outer-sphere and activated complexes which is expected to be approximately unity for the analogous structures of these complexes.

Thus, as far as the above investigations are concerned, the ligand dependences of K_{12} and k_{23} seem to be realistic. However, in view of the small differences in the reaction parameters compared with the statistical uncertainties involved, together with the errors originating from the uncertainties of the complexation constants used,²² it is difficult at present to elucidate the above feature. A

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(22) The variations of K_1 , K_2 , and K_3 within the reported error intervals (the standard errors) yielded the changes of the reaction parameters in the range ±10, ±12, and ±8% for the K_{12} 's and ±6, ±5, and ±3% for the k_{23} 's of the formate, acetate, and propionate systems, respectively.

full interpretation must await further accumulation of the experimental data.

The signs of the volume changes are not determined from the absorption data alone since the square of the linear combination of the volume changes is involved in μ_m ; hence, the signs of the ΔV_{23} 's were taken to be positive on the basis of the electrostriction effect of the metal ion. As shown in Table II, the ΔV_{12} values lie in the narrow range of -0.2 to 2.5 cm³ mol⁻¹, being substantially less than the ΔV_{23} values. They are also much less than the volume change 7–9 cm³ mol⁻¹ reported for the outer-sphere complexing of magnesium and manganese sulfates.^{23,24} However, considering the weak electrostatic interaction for the 2–1 valent ion pairs,^{23,25} together with the effect of the high ionic concentration of the medium,²⁶ the ΔV_{12} 's in Table II are of reasonable magnitude. Table II also shows that the ΔV_{23} value increases almost linearly with the number of hydrocarbon chains of the carboxylate ions. Here, it is interesting to note that the same tendency has also been observed for the volume changes on protonation of the carboxylate ions.²⁷

Through the above investigation, kinetic behaviors of the complexation of zinc(II) formate, acetate, and propionate all proved to be similar; the concentration dependences of the relaxation parameters together with the obtained values of the reaction parameters are wholly consistent with the Eigen-Tamm mechanism. Although the result reveals a feature that the rate of ligand substitution depends on the nature of the ligand, the uncertainties inolved preclude definite conclusion at present. Recently, we studied the complex formation of zinc ion with thiourea, a highly nucleophilic ligand, and noticed that the rate constant of ligand substitution on the metal is 2×10^8 s⁻¹, which is much larger than those of Table II. The detailed result will be reported in due course.

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Stabilities of Substituted Benzyl Radicals: Dissociation Rates of Amino-, Hydroxy-, and Cyanoethylbenzenes

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Rates of the thermal unimolecular decomposition of amino-, hydroxy-, and cyanoethylbenzenes have been determined by the very low pressure pyrolysis technique. Assuming equal A factors, these rates, relative to the rate of dissociation of ethylbenzene, yield the following ortho, meta, and para, respectively, substituent effects on benzylic C-C bond strengths (kcal/mol): NH₂, -2.7, -0.3, -1.7; OH, -1.7, -0.7, -1.1; and CN, -0.3, 0.4, -1.5. These effects are generally smaller than those for substituted anisoles and follow different trends. Along with the results of ESR studies of Nicholas and Arnold (Can. J. Chem. 1986, 64, 270), the present substituent effects indicate that a 1-G change in the benzylic hyperfine coupling constant corresponds to a 1.8 kcal mol⁻¹ change in bond strength.

Introduction

The effect of a substituent on reaction thermodynamics is perhaps the most fundamental of "substituent effects". In freeradical reactions, other factors, most notably "polar effects", are typically deduced from deviations in thermodynamic/rate correlations. A detailed understanding of radical substituent effects therefore requires thermodynamic information.

These thermodynamic effects can be expressed as differences in bond dissociation energies in substituted and unsubstituted molecules, ΔBDE , as illustrated below for benzyl radicals:

 $\Delta BDE = BDE(XC_6H_4CH_2-R) - BDE(C_6H_5CH_2-R) \quad (1)$

In the present work, we report $\triangle BDE$ (R = methyl) values for hydroxy, amino, and cyano substituents. These values are derived

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from differences in dissociation rates of ethylbenzene and substituted ethylbenzenes measured by the very low pressure pyrolysis technique (VLPP).

Earlier studies employed VLPP to determine rates of dissociation of substituted anisoles and methyl-substituted ethylbenzenes.^{1,2} This method is well suited for these measurements because it provides rather precise relative rate constants, and at the low pressures of these experiments, complications from bimolecular reactions are avoided. Results of earlier studies of methyl-substituted ethylbenzenes were in good agreement with the independent determinations of Hayashibara, Kruppa, and Beauchamp,³ who derived substituent effects from thermodynamic cycles involving ions. Results of the anisole studies² agreed quite well with equilibrium constants derived from the condensed-phase studies of Mahoney.⁴

Two effects are of particular interest here. Earlier studies showed that the oxygen-methyl bonds in o-hydroxyanisole and o-aminoanisole were weakened by very large amounts (ca. 7 kcal). We wanted to see whether a similar effect occurred in ethylbenzenes. Also, ESR studies of substituted benzyl radicals indicated large differences in stabilization by a cyano group in the para and meta positions.⁵ In contrast, the cyano group had minimal effects on dissociation rates in anisole.^{2b} We wanted to confirm and quantify this difference between benzyl and phenoxyl substituent effects.

Experimental Details

The apparatus and procedures used in these studies have been described previously.⁶⁻⁸ Briefly, we used a 75-mL cylindrical quartz VLPP reactor with a collision number of $1160.^{1.7,8}$ The reactor temperature could be varied from 298 to 1275 K and was measurable to ± 3 K or less, with a precision of 1 K using chromel-alumel thermocouples placed at the top, center, and bottom of the reactor.

The reactor had two 1-mm gas inlets. Reactants entered through one and an inert gas such as Ar through the other. Products exiting the reactor were analyzed with a quadrupole mass analyzer adjusted to an ionization energy of 70 eV. The heights of the mass spectral peaks were normalized to the peak height of the inert gas. Rates of ethylbenzene dissociation were periodically redetermined to assure reproducibility. The extents of decomposition were reproducible to $\pm 1\%$. Flow rates of reactants were regulated by controlling the temperature, hence vapor pressure, of the condensed-phase reactant (between 0 and 50 °C).

All chemicals used here were obtained from commercial sources and stored in a refrigerator before use. Capillary GC analysis indicated that the compounds were very pure (>98%), and they were used without further purification.

Results

A. Product Analysis. As in previous studies of ethylbenzenes,^{1,7,8} mass spectra of the decomposition products showed a prominent peak at m/e = 15 (methyl radical) and gave the peaks expected from substituted benzyl radicals under VLPP conditions. Moreover, in each compound, the benzylic C-C bond is by far the weakest. We conclude that each of the nine substituted ethylbenzenes studied decomposed by benzylic C-C bond homolysis.

B. Rate Measurements under VLPP Conditions. Unimolecular rate constants under VLPP conditions were calculated from the

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Figure 1. Rate constants for the thermal decomposition of $(\triangle) o$ -, (\blacksquare) *m*-, and (\bullet) *p*-aminoethylbenzene. Solid lines are RRKM fit to the data.



Figure 2. Rate constants for the thermal decomposition of (\blacktriangle) o-, (\blacksquare) m-, and (\bigcirc) p-hydroxyethylbenzene. Solid lines are RRKM fit to the

data.



Temperature (K)

Figure 3. Rate constants for the thermal decomposition of $(\triangle) o_{-}, (\blacksquare) m_{-}$, and $(\bullet) p$ -cyanoethylbenzene. Solid lines are RRKM fit to the data.

extent of disappearance of the reactant by the equation $k_{uni} = k_e(I_0 - I)/I$. Here, I is the mass spectrometer signal intensity of the parent molecular ion with the reactant flowing through the reactor, and I_0 is the intensity with the reactant flowing through the bypass line. The escape rate constat k_e is a function of the reactor geometry and equals $3.965(T/M)^{0.5}$ s⁻¹ for our 3-mm aperture reactor. T is the reactor temperature (K) and M is molecular weight of the reactant.⁶

C. High-Pressure Rate Constants and $\triangle BDE$. The measured rate constants are in the low-pressure regime and so depend on the collision frequency. RRKM calculations were done to convert these to more meaningful high-pressure rate constants. As in previous studies,^{1,7,8} and A factor of log A (s⁻¹) = 15.3 was used in these calculations. Any error in this choice would have little effect on the relative rate constants of concern in this work. The RRKM vibrational models of amino-, hydroxy-, and cyano-

TABLE I: Relative Bond Strengths (kcal mol-1) of Substituted Ethylbenzenes, Toluenes, and Anisoles

	ΔBDE^{a}			$\Delta BDE(O-CH_3)^b$		
subst X	ortho	meta	para	ortho	meta	рага
NH ₂	-2.78	-0.3	-1.7	-7.4	-0.4	-3.0
он⁻	-1.7	-0.7	-1.1	-7.2	0.3	-2.5
CH3	-1.3°	-0.3°	-0.4°	-2.6	-0.5	-1.9
-	-1.9 ^d	-0.4^{d}	-0.6 ^d			
	-3.5°	0.0 ^{e,f}	-2.5°			
CI		1.2^{f}	0.1 ^f		0.2	-1.0
Br		1.2				
CN	-0.3	0.4	-1.5	-0.2	1.1	0.3

^{*a*} For substituted ethylbenzenes except for d-f, which are for tolu-enes. ^{*b*} From ref 2. ^{*c*} From ref 1. ^{*d*} From ref 3. ^{*c*} From ref 10. ^{*f*} From ref 11. ^g Values in boldface are from present experiments.

ethylbenzenes were derived by adjusting the frequencies to match estimated entropies and heat capacities at 1000 K.⁹

In Figures 1-3, the experimental rates and RRKM fits to the data are plotted against temperature. The parallel curvature of each reactant, well reproduced by RRKM calculations, suggests that the reactions are homogeneous and unimolecular. Differences in activation energies are presumed to be equal to differences in bond dissociation energies (i.e., $\Delta E_a = \Delta BDE$). Results from the present and earlier VLPP experiments are summarized in Table L

Also shown in Table I are substituent effects on the C-H bond strength of toluene, ΔBDE (β -CH₂-H), as derived from results of other experiments.^{1-3,10,11} These values are nearly equivalent to $\Delta BDE(\beta$ -C-CH₃). The difference is the enthalpy for the substituent-transfer reaction $XC_6H_4CH_3 + C_6H_5CH_2CH_3 =$ $C_6H_5CH_3 + XC_6H_4CH_2CH_3$, which is expected to be quite small. For the sake of comparison, Table I also includes $\Delta BDE(O-CH_3)$ derived from dissociation of substituted anisoles.²

Discussion

A. Bond Strength Effects. Except for m-cyano, each of the eight substituents on ethylbenzene weakened the benzylic C-C bond. The magnitudes of ΔBDE effects for electron donating groups (amino, hydroxy, and methyl¹ groups) are in the order ortho > para > meta. This ordering is consistent with the simple idea that, in the ortho position, both steric relief and conjugative effects (in the radical) weaken the bond, in the para position, only conjugative effects contribute, while in the meta position neither contributes.

The cyano substituent, considered an electron-withdrawing group, is different. While weakening the bond appreciably from the para position, it has little effect in the ortho position. In the meta position, it actually strengthens the bond slightly. For Cl and Br substituents, which can also be viewed as electron withdrawing, Pryor and co-workers have also reported bond strengthening in the meta position¹¹ but by a somewhat larger amount (1.2 kcal) than that observed here for cyano (0.4 kcal). From the para position, however, unlike p-cyano, Pryor and coworkers reported that Cl had no noticeable effect.¹¹ The effect of a methyl substituent determined in previous VLPP studies¹ has been confirmed by another technique.³ As discussed previously,¹ the significantly greater values of Szwarc¹⁰ may have been caused by mechanistic complexities.

B. Comparison with Phenoxy-Methyl Bond Strengths. For o-methyl and the three electron-donating para substituents, the effects on benzyl are 1.4 ± 0.1 kcal less than on phenoxyl. However, this is not the case for the o-amino and o-hydroxy substituents, which exert exceptional bond weakening effects in anisoles, but not in the ethylbenzenes. For these two substituents,

TABLE II:	Comparison of	ΔBDE with	Activation En	ergies of
Thermolysis	Reactions and	ESR Radical	Stabilization	Energies

		$\Delta BDE/kcal mol^{-1}$			$\Delta SE/kcal mol^{-1}$		
subst X	а	b	С	d	е	d	f
m-CH ₃	-0.3	-0.05			-0.05		
p-CH ₃	-0.4	-0.19	-0.12	-0.97	-0.34	-0.59	0.37
m-CN	0.4	0.21			0.59		
p-CN	-1.5	-0.78		-0.04	-0.89	-1.35	-0.96

^a BDE values from VLPP measurements. Δ SE calculated by using hfcc data^{5,14,16} and eq 2 (see text). ^bFrom ref 13. ^cFrom ref 15. ^d From ref 14. ^e From ref 16. ^f From ref 18.

bond weakening effects in benzyl are smaller than in phenoxyl by 4.7 and 5.5 kcal, respectively.

The electron-withdrawing cyano group in the para position causes a distinct bond weakening in ethylbenzene and a slight bond strengthening in anisole. At the ortho position, it has a very small and similar bond weakening effect in the two molecules. In the meta position, it causes bond strenghtening in both compounds, though the effect is substantially larger in anisole.

The substantial differences in the effects of substituents on benzyl and phenoxyl might be viewed as surprising. Radical sites in both are, in effect, centered on carbon atoms. On the basis of its spin densities, the phenoxy radical is, in effect, a carbonyl-substituted cyclohexadienyl radical.¹² While the generally larger effects observed for the anisoles might be connected with the higher odd-electron density in the ring of phenoxyl radicals than in benzyl radicals,12 this clearly cannot explain the differences of the p-CN, o-OH, and o-NH₂ substituents. The strong stabilization of the latter two ortho substituents in phenoxyl radicals seems to be due to hydrogen bonding between the H atoms on the substituent and the phenoxyl oxygen atom. This effect clearly has no parallel in benzyl radicals. That is, the benzylic radical site cannot form a strong hydrogen bond.

Differences for p-CN however are not readily rationalized. Further, rates of dissociation of para-substituted anisoles² showed little, if any, correlation with Arnold's benzyl substituents constants.^{5,16} These differences deserve theoretical study.

C. Measured $\triangle BDE$ and Rates of Other Dissociation Reactions. For methyl and cyano substituents, literature data for three reactions can also yield $\triangle BDE$ values. These are as follows: (1) the thermal rearrangement of 2-aryl-3,3-dimethylmethylenecyclopropanes,¹³ (2) the dissociation dibenzyl mercurials,¹⁴ and (3) the dissociation of diphenylazomethanes.¹⁵ Relevant ΔBDE values derived from these studies are shown in Table II. They were obtained by assuming that differences in rates are due solely to differences in $\triangle BDE$, the same procedure used in the treatment of our own results.

Creary's results¹³ show the same tends as ours but are generally only half as large. Jackson's results¹⁴ are quite different, showing a sizable bond weakening for p-methyl and little effect for p-cyano. Perhaps in view of the small magnitudes of the effects and the small number of substituents in common, this low level of agreement should have been expected.

D. $\triangle BDE$ and Radical Stabilization Energy. Differences in benzylic hyperfine coupling constants (α -hfcc) of substituted benzyl radicals provide, in principle, a direct measure of differences in radical stabilities.¹⁶ The basic idea behind this relation is that the more stabilizing a substituent is, the more it will withdraw odd-electron density from conjugated positions. In fact, in earlier studies of anisole dissociation, we found a strong correlation between ESR data for substituted phenoxyl radicals¹⁷ and disso-

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ciation rates of substituted anisoles ($\Delta BDE(oxygen-CH_3)$).² Such correlations indicate that contributions to ΔBDE from the stabilities of the molecules are either very small or are proportional to $\triangle BDE$.

On the basis of ESR measurements and the ab initio MO calculations for a number of substituted methyl radicals, Nicholas and Arnold¹⁶ derived the following relationship between the α -hfcc and stabilization energies (SE) of benzyl radicals:

SE (kcal mol⁻¹) =
$$34.6 - 1.37 \times \alpha$$
-hfcc (G) (2)

SE values derived from this expression with literature α -hfcc values from three studies^{14,16,18} are given in Table II. In general, results are in good accord with the present determinations, suggesting, as commonly presumed, that $\triangle BDE$ for benzyl radicals is strongly correlated with radical stability.

From the present $\triangle BDE$ and the Dust and Arnold's ESR data for *m*- and *p*-cyanobenzyl radicals,⁵ we estimate that the ΔBDE increases by 1.8 kcal/unit increase in α -hfcc. This is comparable to the 1.4 kcal proportionality factor between SE and α -hfcc of Nicholas and Arnold (eq 2).

Summary

We determined the effects of amino, hydroxy, and cyano substituents on the benzylic C-C bond strength, ΔBDE , by measuring homolysis rates of substituted ethylbenzenes. The effects varied from +0.4 to -2.7 kcal. Exceptional o-OH and o-NH₂ effects observed previously in anisoles were absent in ethylbenzenes. For electron-donating para substituents (and o-methyl, as well), the magnitude of $\triangle BDE$ in ethylbenzenes was 1.4 ± 0.1 kcal less than in the anisoles. The effect of the electron-withdrawing p-cyano group, on the other hand, was significantly greater in ethylbenzene.

These $\triangle BDEs$ showed mixed agreement with the limited number of values derived from other dissociation rates.13-15 However, there was better agreement with radical stabilization energies derived from ESR (α -hfcc) measurements.^{5,14,17} On the basis of differences in the *m*- and *p*-cyano substituent, we derived a proportionality constant of 1.8 kcal/unit change in α -hfcc, in reasonable agreement with Nicholas and Arnold's value of 1.4 kcal.¹⁶ The similarity of these values supports the common assumption that substituent effects in radical reactions are due primarily to effects on radical, not molecule, stabilities.

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MCSCF Study of the Rearrangement of Nitromethane to Methyl Nitrite

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An ab initio study has been made of the unimolecular rearrangement of nitromethane to methyl nitrite. Geometry optimizations employing the 6-31G* basis have been carried out for nitromethane and methyl nitrite with a two-configuration wave function and for the unimolecular transition state with a 20-configuration wave function. Energies were determined by using a multiconfigurational expansion, including all configurations generated by excitation from the two highest occupied orbitals into the two lowest empty orbitals (four electrons in four orbitals). The transition state indicates a weak interaction between a methyl radical and nitro radical. In the transition state, the breaking CN bond and the forming CO bond are 3.617 and 3.700 Å, respectively, and there is a significant difference predicted in the NO bond lengths in the transition state (1.371/1.155 Å). At the highest level of calculation used in this work (truncated multireference CI), the unimolecular barrier is predicted to be 10.0 kcal/mol above the sum of CH₃ and NO₂ radical energies, which is in conflict with experiment since the unimolecular rearrangement is observed to occur.

Introduction

It has recently been predicted¹ and verified^{2,3} that the unimolecular rearrangement of nitromethane to methyl nitrite might be competitive with simple C-N bond rupture. The predictions were based on MINDO/3 calculations performed by Dewar and co-workers,¹ who found the concerted transition state to have an energy 14.6 kcal/mol lower than the energy of the radicals. When a less favorable entropy for the rearrangement is taken into account, Dewar concluded that the two pathways would be competitive. Recent experimental work³ has led to a confirmation of these predictions. Employing infrared multiple-photon dissociation (IRMPD), Lee and co-workers³ have been able to determine the barrier to be between 51.5 and 57.0 kcal/mol with 55.5 kcal/mol as the most probable value. For comparison, the C-N bond energy in nitromethane is determined to be 59.4 kcal/mol.4

The experimental results above contrast sharply with previous ab initio results⁵ where the unimolecular rearrangement barrier to CH₃ONO was found to be 16.1 kcal/mol higher than the C-N bond energy in CH₃NO₂ (73.5 and 57.4 kcal/mol, respectively). The calculations were performed using the 6-31G* basis⁶ to determine geometries and zero-point corrections and the MP2/6-31G* electron correlation treatment⁶ on 6-31G* optimized geometries to determine relative energies. It was anticipated that the method would poorly describe the unimolecular transition state since it was based on a single-determinant wave function while

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