Table XIII. Calculated NPE Contributions to Relative Rate Constants for S_N2 Reactions of Methyl Bromide with Hydroxide or Alkoxide Ions at 298 K

alkyl group R in the alkoxide ion	$k(R)/k(Me)$	MMI	EXC	ZPE
H	1.856	189.9	0.054	0.180
Me	1.000	1.000	1.000	1.000
Et	0.996	0.362	2.269	1.213
i-Pr	0.992	0.196	3.672	1.380
t-Bu	0.989	0.135	4.872	1.499

and those from ZPE and EXC on the other. We encountered a similar pattern of results in calculations for E2 reactions with ethyl chloride and a range of homologous bases, and we give a detailed analysis of these results in the following paper:[24] the calculations on substitutions were in fact prompted by the results on eliminations. Much of our analysis of the elimination results is

transferable to those for substitutions, so only brief interpretative comments are here in order.

Loss of translational and rotational entropy in association is less for the lighter nucleophiles, and this is particularly true for loss of rotational entropy in the reaction with hydroxide, which not only is a relatively very light rotor but also has only two moments of inertia. These considerations in essence underly the variation of the MMI term. The opposition for EXC and ZPE is related to the relatively higher frequencies in the new vibrational modes of the transition states the lighter the mass of the associting base, and again the hydroxide–methoxide transition is the most marked.

If we leave the hydroxide result aside, because of the relatively very large change in mass distribution and structure between hydroxide and methoxide, and concentrate attention on the results for the series of alkoxides, it is evident that base homology is very much less effective in inducing overall relative NPE effects than in substrate homology as studied in the Finkelstein calculations. The difference seems to be due to the fact that substrate alkylation is associated with changes in geometry and force constants around the reaction site, whereas base homology is not in our calculations.

(24) C. D. Chalk, J. McKenna, L. B. Sims, and I. H. Williams, following paper in this issue.

NPE Effects in Bimolecular Elimination

Christine D. Chalk, James McKenna,* Leslie B. Sims, and Ian H. Williams

Contribution from the Department of Chemistry, The University, Sheffield S3 7HF, England. Received December 6, 1979

Abstract: A force field for the transition states of E2 reactions between hydroxide and alkoxide bases and simple chloroalkanes has been developed by calibration against typical experimental kinetic isotope effects observed in such reactions and forms the basis of calculations of NPE effects. No allowances are made for steric effects associated with alkylation in the substrate or base. With this model force field only slight NPE contributions to relative reactivity are observed from homology among substrates (ethyl vs. isomeric propyl chlorides) or among alkoxide bases. A more substantial difference is observed in a comparison of hydroxide and methoxide ion promoted eliminations from ethyl chloride.

Introduction

As part of a survey of the role of nonpotential energy (NPE) effects in reactivity, we have previously discussed some bimolecular nucleophilic substitutions[1] and we now report the results of calculations for some simple examples from another very important class of organic reactions, namely, bimolecular elimination.[2]

NPE effects, like kinetic isotope effects, may be analyzed[1] in terms of three multiplicative factors, MMI, EXC, and ZPE, describing contributions (relative to a standard reaction) from masses and moments of inertia, population of excited vibrational energy levels, and vibrational zero-point energies, respectively. If a reaction involves changes in vibrational modes having average to high frequencies, then the ZPE term would be expected to dominate the vibrational contributions to NPE effects. However, as the frequencies involved in any changes become lower, so the importance of EXC will increase, until for very low frequencies it will become the dominant term. This behavior arises because of the inverse exponential dependence on frequency of the vibrational partition function. The exponential character of EXC may be contrasted with the linear relationship between ZPE and frequency changes and underlies a hypothesis that for suitable

systems EXC could take extremely large values which could have substantial accelerating or retarding effects on reactivity. Some possible implications of this hypothesis have already been suggested for enzymic catalysis,[3a] and our calculations[3b] on simple enzyme models and on reactions within solvent cages do indeed show large and dominant EXC contributions. For gas-phase type calculations of the usual reactions of normal small molecules, however, a more even balance between the three factors may be expected. This was found to be the case for calculations on some S_N2 substitutions,[1] and another such pattern is now described for E2 eliminations.

Calculations

All calculations were performed by using program QREL and previously described methods.[1,4,5] The simplest reaction studied was the hydroxide ion promoted elimination from chloroethane to yield ethylene, and a suitable transition-state model for this parent system was found which enabled kinetic isotope effects to be calculated within the ranges of observed values. More complex

(1) C. D. Chalk, J. McKenna, and I. H. Williams, preceding paper in this issue.

(2) W. H. Saunders, Jr., and A. F. Cockerill, "Mechanisms of Elimination Reactions", Wiley, New York, 1973.

(3) (a) D. B. Cook and J. McKenna, *J. Chem. Soc., Perkin Trans. 2*, 1223 (1974). (b) C. D. Chalk and J. McKenna, unpublished results.

(4) C. D. Chalk, B. G. Hutley, J. McKenna, L. B. Sims, and I. H. Williams, preceding paper in this issue.

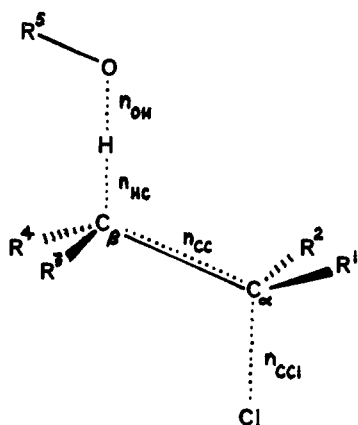(5) J. McKenna, L. B. Sims, and I. H. Williams, preceding paper in this issue.

Figure 1. Schematic transition state for bimolecular elimination.

reactions involved alkylation either of the chloroethane substrate or of the base, and the transition states for these reactions, shown in Figure 1, all involved the same structural parameters and bond orders as the parent hydroxide ion/chloroethane system.

The reactant geometries employed the same idealized bond lengths, tetrahedral interbond angles, and staggered conformations specified for chloroalkanes,[4] with the addition of two extra parameters, bond lengths of 1.47 Å for C–O and 0.958 Å for O–H. Transition-state bond lengths r_{XY} were obtained from reactant values $r°_{XY}$ by application of Pauling's rule as used by Sims and co-workers,[6] where n_{XY} is the bond order.

$$r_{XY} = r°_{XY} - 0.30 \ln (n_{XY}) \qquad (1)$$

Force constants for reactants were obtained directly from the model force field for chloroalkanes:[4] for the specification of some bending and torsional coordinates the oxygen atom of the base was regarded as a carbon atom. Transition-state force constants were obtained from the reactant values by the application of empirical rules relating force constant changes to changes in bond order and geometry.[5,6] The additional force constants required for reactant and transition-state coordinates involving the oxygen atom are as follows. Stretching force constants (mdyn Å^{-1}): O–H, 7.8; C–O, 5.3. Bending force constants (mdyn Å rad^{-2}): HCO, CCO, 1.0; HOH, COH, 0.76; OHC$_\beta$, 0.32; τ(C–O), 0.027; τ-(O···H···C$_\beta$), 0.005. Many of these values were derived from quantum mechanical[7] or spectroscopic[8] force constants for methanol. The linear bending force constant for the coordinate OHC$_\beta$ is similar to values used by Sims[6] and Saunders[9] and falls in the range 0.3–0.4 found for other examples of such force constants.[10] The torsional force constant τ(C–O) was such as enabled the observed methanol torsional frequency to be reproduced, and the torsional force constant τ(O···H···C$_\beta$) was determined as that value which led to the calculated entropy for this harmonic vibration being equal to the calculated entropy of free internal rotation about the O···H···C$_\beta$ axis. The transition-state torsional force constants τ(C$_\alpha$–C$_\beta$) were given the same values as in the reactants: they were not allowed to vary with the C$_\alpha$–C$_\beta$ bond order.

Kinetic Isotope Effects

A series of kinetic isotope effects was calculated for the E2 hydroxide ion/chloroethane reaction with an antiperiplanar transition state involving tetrahedral interbond angles. The total bond orders of the reactants and of the transition state were assumed to be equal such that the increase in bond order due to

Table I. Calculated Kinetic Isotope Effects for Bimolecular Elimination from Chloroethane with Hydroxide Ion at 298 K

isotopic substn	KIE^a	MMI	EXC	ZPE
D^b	5.443	1.066	1.012	5.049
α-d_2^{c}	1.105	1.061	0.941	1.106
β-d_2^{c}	0.940	1.054	1.009	0.883
α-^{14}C	1.016	1.030	0.973	1.014
β-^{14}C	0.996	1.054	0.972	0.972
^{37}Cl	1.003	1.009	0.992	1.002

^{a} KIE = k(light)/k(heavy). ^{b} Primary. ^{c} Secondary.

Table II. Calculated NPE Contributions to Relative Rate Constants for E2 Reactions of Hydroxide Ion with Substituted Chloroethanes at 298 K

substrate RCl	k(R)/k(Et)	MMI	EXC	ZPE
Et	1.000	1.000	1.000	1.000
gauche n-Pr	1.090	0.763	1.068	1.339
anti n-Pr^a	0.862	0.814	0.940	1.126
i-Pr	0.826	0.745	1.350	0.871

^{a} Internal rotation gives antiperiplanar transition state for elimination.

bond making was balanced by the decrease due to bond breaking. Assignment of a bond order x to the partial O···H bond between the base and the substrate in the transition state enabled the bond orders of all the bonds participating in the reaction coordinate to be determined: $n_{O···H}$, x; $n_{H···C_\beta}$, $1 - x$; $n_{C_\beta-C_\alpha}$, $1 + x$; $n_{C_\alpha···Cl}$, $1 - x$. The calculated isotope effects were found to vary with the value chosen for x; a value of $x = 0.4$ resulted in a near maximum primary deuterium isotope effect and was used in all subsequent calculations. The reaction-coordinate mode was generated by introducing interaction force constants between bond stretching coordinates such that compression of the (making) O···H and C$_\beta$–C$_\alpha$ bonds was coupled with extension of the (breaking) H···C$_\beta$ and C$_\alpha$···Cl bonds. Consideration of the optimum conditions for reproduction of kinetic isotope effects led to these interaction force constants being assigned values (mdyn Å^{-1}) of 2.966, for O···H/H···C$_\beta$, 1.438, for H···C$_\beta$/C$_\beta$–C$_\alpha$, and 1.120, for C$_\beta$–C$_\alpha$/C$_\alpha$···Cl. These values, which are similar to a set used by Saunders,[9] produced an imaginary frequency of 690i cm^{-1} for the reaction-coordinate mode and were subsequently used to generate the reaction-coordinate modes in calculations of NPE effects for more complex reactions.

The calculated kinetic isotope effects are presented in Table I; all values lie satisfactorily within the ranges of appropriate experimental values.[2] It is of interest, however, to note that the normal chlorine isotope effect of 1.003 for $^{35}k/^{37}k$ has a large contribution of 1.009 arising from the MMI term.

Effect of Substrate Alkylation

The parent E2 hydroxide ion/chloroethane reaction was modified by methylation of the substrate in various positions. Calculated NPE contributions to relative rate constants at 298 K are presented in Table II for eliminations from these substituted chloroalkanes with respect to that for the unsubstituted chloroethane. It may be seen that with the models chosen substrate methylation has very little effect on NPE contributions to relative rate constants; this result contrasts with the range of 30 times found between the fastest and slowest of S_N2 reactions involving alkylated substrates.[1] The difference in results from the two sets of calculations is probably mainly due to the circumstance that we explicitly allowed for the variable steric effects from alkylation in specifying the substitution transition states but have not (so far) done this for the eliminations. Steric forces are not expected to restrict motions of atoms in reacting bonds in the less crowded transition states for elimination as they do in the more crowded substitution transition states. In the case of elimination, therefore, an approximate separation of normal modes may be made between those involving the alkyl substituent and those involving the reacting bonds, in a manner analogous to that described by Wolfsberg.[11]

(6) G. W. Burton, L. B. Sims, J. C. Wilson, and A. Fry, *J. Am. Chem. Soc.*, **99**, 3371 (1977).

(7) (a) Tae Kyu Ha, R. Meyer, and Hs. H. Günthard, *Chem. Phys. Lett.*, **22**, 68 (1973); (b) E. Taillander and D. J. David, *Chem. Phys.*, **4**, 157 (1974).

(8) (a) P. D. Maillinson and D. C. McKean, *Spectrochim. Acta, Part A*, **30A**, 1133 (1974); (b) P. D. Mallinson, *J. Mol. Spectrosc.*, **58**, 194 (1975).

(9) W. H. Saunders, *Chem. Scr.*, **8**, 27 (1975).

(10) J. C. D. Brand and J. C. Speakman, "Molecular Structure: The Physical Approach", Arnold, London, 1960.

NPE Effects in Bimolecular Elimination

J. Am. Chem. Soc., Vol. 103, No. 2, 1981 283

Table III. Calculated NPE Effects on Relative Rate Constants for E2 Reactions of Chloroethane at 298 K Promoted by Hydroxide and Alkoxide Ions

alkyl group R in the alkoxide ion	$k(R)/$ $k(Me)^a$	MMI	EXC	ZPE
H	4.069	239.6	0.058	0.293
Me	1.000	1.000	1.000	1.000
Et	1.112	0.202	3.661	1.507
i-Pr	0.956	0.100	6.683	1.425
t-Bu	1.018	0.065	9.808	1.584
n-Pr	1.009	0.102	6.772	1.469
i-Bu	1.009	0.064	10.278	1.540
neo-Pe	0.841	0.049	11.521	1.495

^{a} Excluding contributions from rotational symmetry number differences.

Variation of Transition-State Geometry

The possibility that NPE effects might help to determine a preference between anti and syn elimination was investigated by variation of the dihedral angle between the leaving group and the hydrogen atom being attacked by the base in the transition state. NPE effects did not produce any significant difference between rate constants calculated for antiperiplanar and synperiplanar transition states. This apparent lack of sensitivity to changes in dihedral angle may be due to the fact that the same force constants were used in the calclations for each of these transition states. This assumption is probably none too realistic, but the calculations may not be easily improved since the manner in which the force constants would change is unknown.[12]

The bond orders chosen for the making and breaking bonds correspond to a transition-state model of roughly central E2 character, but transition-state geometries with tetrahedral interbond angles were employed throughout. Departure from tetrahedral (sp³-hybridized) geometry toward trigonal (sp²-hybridized) geometry about atoms C_α and C_β had little effect on calculated NPE contributions to relative reactivity, even though bending force constants were appropriately modified in accord with the geometrical changes by means of a preiously described empirical rule.[5,6]

Effect of Alkylation of Base

Table III contains calculated NPE contributions to relative rate constants for alkoxide ion promoted E2 reactions of chloroethane with respect to the reaction with methoxide as standard, excluding effects arising from differences in rotational symmetry numbers of the bases. Again, as indicated above, no allowance was made in the calculations for varying steric demands of the bases in the transition states, and perhaps mainly because of this factor (cf. S_N2 results in ref 1) there are little overall NPE effects for reactions with different alkoxide ions. The relative rate constants of near unity value for reactions with different alkoxide ions arise in each case, however, from a remarkable compensation of MMI, EXC, and ZPE terms. Additionally, notwithstanding the simplicity of the transition-state models, the rate constant for the hydroxide reaction is markedly different from that of the alkoxides. The main value at the present time of the results in Table III is the glimpse they give us of the unexpectly large contributions to comparative chemical reactivity from the three NPE components, and the extent to which these can in a suitable system substantially balance one another.

From Table III we see that NPE effects accelerate the hydroxide ion reaction by a factor of 4 over that for methoxide, and that this increase in rate arises from a very large MMI term which is offset by considerably retarding EXC and ZPE terms. The

Table IV. Analysis of Changes in Numbers of Degrees of Freedom in Associative Processes

| reactants^a | product^a | change in the no. of degrees of freedom | | |
		trans	rot.	int
M + M	L	-3	+2	+1
M + L	L	-3	0	+3
M + L	NL	-3	+1	+2
M + NL	NL	-3	0	+3
L + L	L	-3	-2	+5
L + L	NL	-3	-1	+4
L + NL	NL	-3	-2	+5
NL + NL	NL	-3	-3	+6

^{a} M = monoatomic; L = linear; NL = nonlinear.

associative process for the bimolecular reactions involves a reduction in the number of degrees of freedom of rotational motion and consequently a decrease in the rotational partition function between reactants and transition state. However, the decrease in the rotational partition function (or the change in rotational free energy) is very much less for the hydroxide ion reaction than for the methoxide (or other alkoxide) ion reactions because the rotational partition function of the reactant hydroxide ion is itself extremely small. There are two reasons for the low value of this partition function: first, the moments of inertia of the hydroxide ion are numerically very small since they are effectively determined only by the rotation of a hydrogen atom about an oxygen atom; second, the hydroxide ion, being diatomic, has only two moments of inertia whereas all other alkoxide bases have three. Therefore the product of the principal moments of inertia, which is the quantity important for determining the rotational partition function, is very much less for hydroxide ion than for any other alkylated base. The lighter mass of the hydroxide ion is an accelerating factor in the bimolecular reaction with respect to that for methoxide, but the very large acceleration is due to the changes in moments of inertia.

Although the associative process involves loss of translational and rotational degrees of freedom, there are compensating gains in internal degrees of freedom. The extra vibrational modes in the elimination transition states have higher frequencies for the hydroxide reaction than for the methoxide reaction since the hydroxide ion is much lighter; in particular, the frequency for the bending mode HO···H is much higher than that of the corresponding mode CO···H. For both reactions the existence of an imaginary reaction-coordinate frequency results in the zero-point energy of the transition state being less than that of the reactants but this decrease is partly compensated for by the extra vibrational frequencies. The higher frequencies in the transition state for the hydroxide reaction ensure a smaller decrease in zero-point energy than for the other reactions and hence give rise to a retarding ZPE term. However, the extra vibrational modes include some with very low frequencies, which are lower for the transition states involving the heavier alkoxide ions, and moreover the associative process in these latter reactions involves the gain of six extra vibrational modes whereas only five are gained in the hydroxide reaction. Thus the vibrational partition functions are much greater for these heavier transition states, and consequently the EXC term retards the hydroxide reaction significantly with respect to the other reactions.

An analysis of changes in numbers of degrees of freedom for different associative processes is given in Table IV. The interesting comparative figures for hydroxide- and alkoxide-promoted E2 reactions prompted us to make a similar comparison (hydroxide/methoxide) for S_N2 reactions of methyl bromide. The calculated pattern[1] is of the same type as that obtained for the eliminations, although the rate constant ratio (1.856) is not so large.

Orientation of Elimination

Calculations of NPE effects in hydroxide-ion promoted bimolecular eliminations of 2-chlorobutane were performed in order to ascertain whether these terms could have any influence upon

(11) Cf. M. Wolfsberg, *Tetrahedron Lett.* **3405** (1964).

(12) A particular difficulty is the prediction of torsional force constants (cf. ref 5); note that the synperiplanar conformation cannot be the transition state both for elimination and for internal rotation, since a single transition state may not connect three "valleys" on a harmonic potential energy surface.[13]

(13) J. N. Murrell and K. J. Laidler. *Trans. Faraday Soc.*, **64**, 371 (1968).

the preferred orientation of the reactions. We calculated relative contributions at 298 K to the rate constants for Saytzeff elimination to but-2-ene and Hofmann elimination to but-1-ene. The force constants for 2-chlorobutane were as specified by the model force field[4] and those for the antiperiplanar transition states were obtained by the methods described above: the bond orders of the making and breaking bonds and the parameters for the reaction-coordinate mode were exactly as those for the reaction of chloroethane with hydroxide ion. A relative rate constant k-(Saytzeff)/k(Hoffman) of 1.087 was obtained,[14] confirming the

view that the generally much larger ratios observed experimentally are related to various potential energetic considerations.[2,15]

Further work with a wider range of E2 transition-state models, including solvation shells, is evidently required and is in hand.

Acknowledgment. We thank the S.R.C. for support.

A Theoretical Approach to the Birch Reduction. Structures and Stabilities of Cyclohexadienes

Arthur J. Birch, Alan L. Hinde, and Leo Radom*

Contribution from the Research School of Chemistry, Australian National University, Canberra, A.C.T. 2600, Australia. Received June 23, 1980

Abstract: Ab initio molecular orbital calculations have been carried out on 1,3-cyclohexadiene (1,3-CHD), 1,4-cyclohexadiene (1,4-CHD), and substituted systems with substituents CH_3, CN, NO_2, F, OH, and NH_2. 1,3-CHD is indicated to be nonplanar with C_2 symmetry while 1,4-CHD is planar with D_{2h} symmetry. The energy difference between 1,3-CHD and 1,4-CHD is small. For substituted cyclohexadienes, the favored isomer is always the 1-substituted 1,3-CHD. Comparison of the energy data for the cyclohexadienes with previously calculated molecular electrostatic potentials for substituted cyclohexadienyl anions suggests that the thermodynamically favored and kinetically favored sites of protonation in the cyclohexadienyl anions frequently differ.
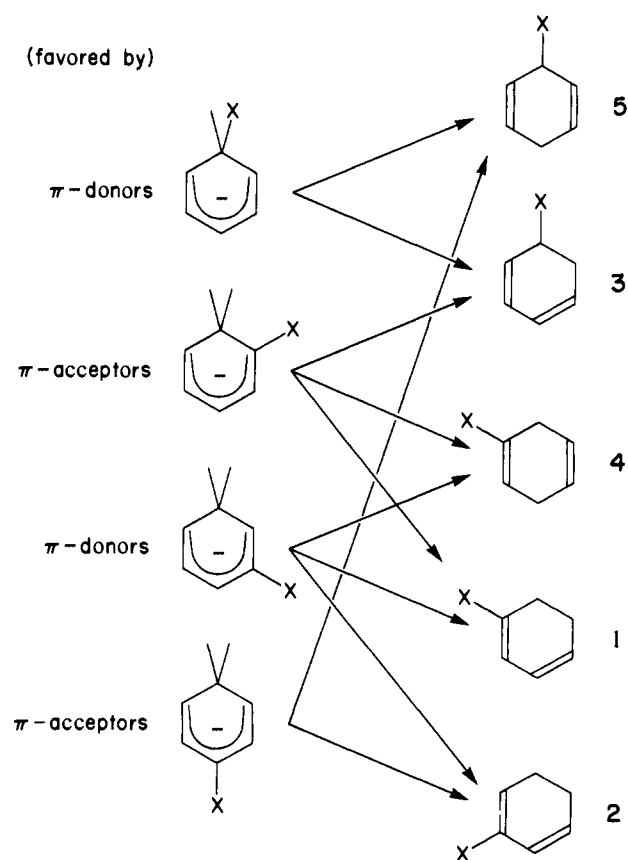
Introduction

A reaction of widespread synthetic utility is the Birch reduction of substituted benzenes by alkali metals and alcohols in liquid

(1)
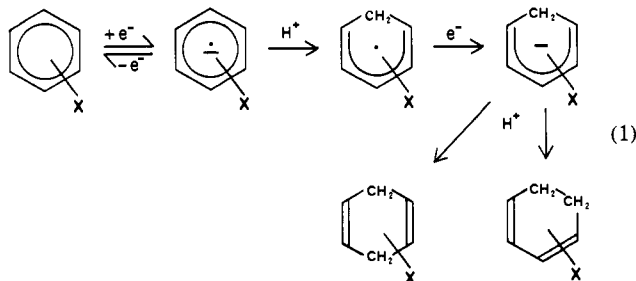
ammonia (eq 1).[1] In recent papers,[2-5] we have examined species involved in the first three steps of the reaction sequence (1). In this paper, we examine the final step of the reaction sequence, namely, the protonation of the cyclohexadienyl anions (CHD⁻'s) to yield a 1,3-cyclohexadiene (1,3-CHD, structures 1–3) or a 1,4-cyclohexadiene (1,4-CHD, structures 4, 5). 1,4-CHD's are formed under irreversible Birch reduction conditions (such as in the presence of an alcohol and with use of, for example, NH_4Cl

Scheme I

(1) Reviews: (a) Birch, A. J.; Subba Rao, G. *Adv. Org. Chem.* **1972**, *8*, 1; (b) Smith, M. In "Reduction", Augustine, R. L., Ed.; Marcel Dekker: New York, 1967; (c) Smith, H. "Organic Reactions in Liquid Ammonia"; Wiley-Interscience: New York, 1963; (d) Cram, D. J. "Fundamentals of Carbanion Chemistry"; Academic Press: New York, 1965; (e) Kaiser, E. T.; Kevan, L., Eds. "Radical Ions"; Interscience: New York, 1968; (f) Harvey, R. G. *Synthesis* **1970**, *4*, 161; (g) Caine, D. *Org. React. (N. Y.)* **1976**, *23*, 1; (h) House, H. O. "Modern Synthetic Reactions"; W. A. Benjamin: Menlo Park, 1972.
(2) Hinde, A. L.; Radom. L.; Poppinger. D. *J. Am. Chem. Soc.* **1978**, *100*, 4681.
(3) Birch, A. J.; Hinde, A. L.; Radom, L. *J. Am. Chem. Soc.* **1980**, *102*, 3370.
(4) Birch, A. J.; Hinde, A. L.; Radom, L. *J. Am. Chem. Soc.* **1980**, *102*, 4074.
(5) Birch, A. J.; Hinde, A. L.; Radom, L. *J. Am. Chem. Soc.* **1980**, *102*, 6430.

to quench the reaction) by protonation of the CHD⁻ at the 3-position (i.e., para to the first protonation site). We have examined this previously[5] with the aid of theoretical molecular electrostatic potentials. 1,3-CHD is a conjugated diene and is thermodynam-