In order to find the cause for the above difference we compare the indazole fluorescence spectra with those of 1-methylindazole and 2-methylindazole. The indazole spectrum obtained in acetic aid is closer to that of 2-methylindazole rather than that of 1-methylindazole, whereas in the other solvents studied here the indazole spectra resemble that of 1-methylindazole. These observations are suggestive of the conversion of indazole in acetic acid from the 1H form to the 2H form in the S_1 state. In acetic acid indazole probably forms a hydrogen bonded complex such as shown in Figure 3. A double proton switching along the hydrogen bonds converts 1H to 2H by the scheme shown in Figure 3.

More definitive evidence for the occurrence of such proton transfer tautomerism is provided by analysis of the fluorescence rise and decay curves. In Figure 4 we give the fluorescence rise and decay curves of indazole in acetic acid observed at different wavelengths. Curve a was obtained by monitoring the fluorescence at 310 ± 10 nm where 1H gives the maximum emission. Curve b was obtained by collecting emissions with wavelength longer than 350 nm. In this case the emission is mostly due to 2H. It is seen that the emission of 1H quickly decays while that of 2H shows a gradual rise. In the other solvents studied here emissions show only exponential decays as shown in Figure 4C.

We have analyzed the observed rise and decay curves based on the scheme shown in Figure 3. Here k_{f1} and k_{f2} are the decay rate constants of the excited singlet states of 1H and 2H, respectively. k_{PT} is the rate constant for proton transfer from 1H to 2H. Solving the appropriate rate equation, we obtain the time dependence of the fluorescence intensity as[17]

$$I(t) \propto \int_0^t P_0(t)[\exp(k_{f2} - k_r)t - 1] \exp(-k_{f2}t)\, dt$$

where $k_r = k_{f1} + k_{PT}$ and $P_0(t)$ is the intensity of the excitation pulse. We have simulated curves a and b with the above equation with $k_{f2} = 8.0 \times 10^8$ s^{-1} and $k_r = 3.1 \times 10^9$ s^{-1}. Decay curve c gives $k_{f1} = 3.6 \times 10^8$ s^{-1}. Because of the ~20-nm bandpath of the 310-nm filter and the slight overlap of the spectra of 1H and 2H, decay curve a has a small contribution from 2H. This contribution was taken into consideration in simulating curve a. As shown in Figure 4B excellent agreement between the experimental and simulated curves was obtained, supporting the scheme given in Figure 3. From the k_{f1} obtained in ethanol k_{PT} is estimated to be 2.7×10^9 s^{-1} at 20 °C. The tautomerization takes place only in acetic acid and not in other protic solvents such as ethanol. Tautomerization is considered to proceed via double proton switching in the hydrogen-bonded complex shown in Figure 3.

Further investigations at various temperatures and in different carboxylic acids are currently in progress.

Registry No. 1*H*-Indazole, 271-44-3.

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Theory of Intramolecular Electron Transfer Reactions in Anion Radicals of Nitrobenzyl Halides

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Recently, we have suggested a lattice-based theory of chemical reactivity in which quantum and statistical mechanical arguments are combined to yield a method for calculating rate constants for certain classes of reactions. We present here the first concrete application of this theory and calculate the first-order rate constants for dehalogenation of the ortho-, meta-, and para-substituted nitrobenzyl chloride anion radicals. Our theoretical results are obtained by calculating the π orbital spin populations of the anion radicals (MO calculations using the GAUSSIAN 82 series of programs), using the consequent values to distinguish the ortho, meta, and para sites, and then calculating the rate constants using a lattice statistical approach, the latter based on a theory presented recently. Apart from the limitations of the MO calculations and the neglect of solvent effects, the method involves no further assumptions or parameters. The theoretical estimates are in good agreement with the experimental rate constants.

One-electron reduction of nitrobenzyl chloride produces the anion radical which subsequently undergoes dehalogenation via an intramolecular electron transfer reaction:[1]

$$\mathrm{O_2NC_6H_4CH_2Cl} \xrightarrow{e^-} \mathrm{^-O_2\dot{N}C_6H_4CH_2Cl} \rightarrow \mathrm{Cl^- + O_2NC_6H_4\dot{C}H_2}$$

The added electron is believed to delocalize over the π system of the nitro group and the benzene ring and is then transferred to the C–Cl σ bond. On the basis of their experimental studies, Neta and Behar suggest that the rate of dehalogenation depends on (1) the degree of overlap between the π system and the σ bond and (2) the steric configuration of the C–Cl bond relative to the plane of the benzene ring.

Recently, we have suggested a lattice-based theory of chemical reactivity[2] in which quantum and statistical mechanical arguments are combined to yield a method for calculating rate constants for certain classes of reactions. We present here the first concrete application of this theory and calculate the first-order rate constants for dehalogenation of the ortho-, meta-, and para-substituted nitrobenzyl chloride anion radicals. Our theoretical results are obtained by calculating the π orbital spin populations of the anion radicals (MO calculations using the GAUSSIAN 82 series of programs), using the consequent values to distinguish the ortho, meta, and para sites, and then calculating the rate constants using a lattice statistical approach (described below), the latter based on the theory presented in ref 3 and 4. Apart from the limitations of the MO calculations and the neglect of solvent effects, the method involves no further assumptions or parameters.

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TABLE I: A Comparison of Experimental vs. Theoretical Rate Constants for One-Electron Reduction of Nitrobenzyl Halides

site	k, s^{-1} (exptl)	k/k(para) (exptl)	π spin population	$\langle n \rangle \sim \tau$	$\langle n \rangle^{-1}/\langle n \rangle^{-1}$(para)	π spin population (normalized)	$\langle n \rangle \sim \tau$	$\langle n \rangle^{-1}/\langle n \rangle^{-1}$(para)
			Series I. Trajectories Initiated from All Possible Sites of the Reaction Space					
ortho	1.0×10^4	2.5	0.10191[a]	1703.85	1.0	0.8712	282.836	1.1
			0.14274[b]	1243.53	1.0	0.8660	283.966	1.1
para	4.0×10^3	1.0	0.11698[a]	1706.53	1.0	1.0000	318.554	1.0
			0.16483[b]	1249.91	1.0	1.0000	318.554	1.0
meta	<5	$<1.3 \times 10^{-3}$	0.00209[a]	85464.6	2.0×10^{-2}	0.0179	10081.2	3.2×10^{-2}
			−0.08780[b]	$>1.8 \times 10^7$	$<1.0 \times 10^{-4}$	−0.5327	$>1.8 \times 10^7$	$<1.8 \times 10^{-5}$
			Series II. Trajectories Initiated from Site of Electron Attachment (on Nitrogen Atom)					
ortho	1.0×10^4	2.5	0.10191[a]	1699.1	1.0	0.8712	278.081	1.3
			0.14274[b]	1238.78	1.1	0.8660	279.211	1.3
para	4.0×10^3	1.0	0.11698[a]	1751.09	1.0	1.0000	361.168	1.0
			0.16483[b]	1294.47	1.0	1.0000	361.168	1.0
meta	<5	$<1.3 \times 10^{-3}$	0.00209[a]	85498.2	2.1×10^{-2}	0.0179	10114.8	3.6×10^{-2}
			−0.08780[b]	$>1.8 \times 10^7$	$<1.0 \times 10^{-4}$	−0.5327	$>1.8 \times 10^7$	$<2.0 \times 10^{-5}$

[a] The π orbital spin populations determined from extended Hückel calculations. [b] The π orbital spin populations determined from INDO calculations. Notice that the INDO calculation gives a π orbital spin population at the meta position which is negative; the calculation of $\langle n \rangle$ in this case was carried out with an effective trap depth of 0.00001.

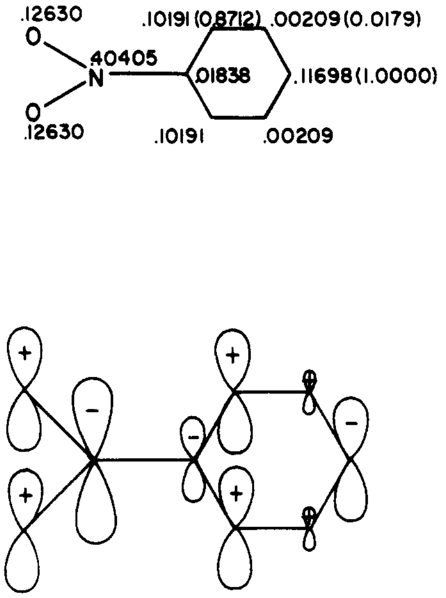

Figure 1. π orbital spin populations at various sites on the nitrobenzyl anion radical. The values noted in the uppermost part of the figure are the π orbital spin populations as determined via an extended Hückel calculation; the numbers in parentheses refer to the values at the ortho, meta, and para positions normalized with respect to the value calculated for the para position. Corresponding INDO calculations of the π orbital spin population values (and normalized values) at the ortho, meta, and para positions yield, respectively, 0.14274 (0.8660), −0.08780 (−0.5327), and 0.16483 (1.0000). Note that the highest occupied molecular orbital (HOMO) is a π orbital for which the occupation at the ortho and para positions is significantly greater than that at the meta positions; thus more of the unpaired electron is localized at the ortho and para sites than at the meta sites, just what one would expect from an examination of the resonance structures of the transition state of the anion radicals.

The physical chemical ideas underlying our approach will now be described. The time scale over which the C–Cl bond breaks (for all three anion radicals studied in ref 1) is such that the delocalization of the attached electron certainly occurs long before the subsequent chemical event, the rupture of the σ bond. Thus the π orbital spin populations of the anion radical listed in Figure 1 may be taken as the (average) electronic environment characterizing sites on the radical. In particular, on a time scale which is long with respect to the initial electron attachment but short with respect to the chemical event, the extended Hückel and INDO calculations reported in Figure 1 quantify the probability of the electron's being at the ortho, meta, and para positions on the anion radical.

Suppose now we regard the chemical event to occur as a result of a local fluctuation in the electron probability density such that on the time scale of such a fluctuation an enhancement occurs in the electron density at one of the ring positions. Given that (on the average) the π orbital spin population is highest at the para position on the ring, it would seem most probable that such a fluctuation would lead to σ-bond breakage at that site, followed by the ortho position, and lastly at the meta position. What is needed to translate this idea into a rate is a means of determining the time scale on which such a fluctuation might occur at each of the three ring positions.

To deal with this, suppose we retreat to a "semiclassical" description of the electron. If on a time scale (much) shorter than the chemical event we regard the electron as a particle migrating from site to site on (and/or in the immediate vicinity of) the anion radical, then the *mean* lifetime τ of the electron before reaction occurs at, say, the para site can be determined by calculating the ensemble average of all possible displacements of the electron, starting from some initial position (e.g., the site of electron attachment) or, given delocalization, from all possible positions defining the reaction space of the system, before its trajectory terminates at the para position. Since the probability of bond breakage depends on the π orbital spin populations characterizing (on the average) the three ring positions and since the above lifetime τ reflects the probability of terminating (on the average) at a given site, the overall averaging problem reduces to the statistical mechanical one of calculating the average walk length $\langle n \rangle$ (a measure of the mean lifetime τ) for random walks on a (micro) lattice with "traps". The trap depths at the three ring positions are assigned by using the probabilities listed in Figure 1. The calculations of $\langle n \rangle$ can be carried out either by brute force Monte Carlo simulation or by mobilizing a recently introduced approach wherein the theory of finite Markov processes is coupled with group theoretic arguments to calculate *exactly* the mean, variance, skewness, and kurtosis of the probability distribution function.[3,4] The latter, analytic theory will be used here and the lattice statistical problem can be solved *exactly* provided we specify the underlying lattice.

We regard the structure of the anion radical as defining a lattice of molecular dimensions. Such a lattice will be most appropriately described as hexagonal, with the nitrobenzyl anion lying in the plane and the C–Cl bond perpendicular to that plane. The latter, out-of-plane bond requires that we embed the anion radical in a space of three dimensions (see Figure 2). To allow for "through space" as well as "through bond" effects, we admit the possibility that sites which are nearest-neighbor sites to the anion radical are also accessible to the electron. (We have performed calculations to assess the *relative* importance of these two effects and the results will be reported elsewhere.) Two sorts of initial conditions are considered here: in a first series of calculations, we assume complete delocalization of the electron and initialize

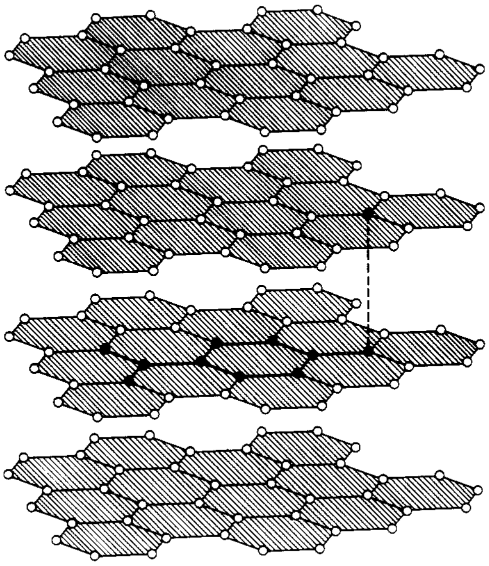

Figure 2. Reaction space of the para-substituted nitrobenzyl chloride anion radical, modeled as a layered hexagonal array of molecular and nearest-neighbor sites. The vertical spacing is not to scale.

trajectories from all possible sites of the reaction space of the system; then, in a second series of calculations, we suppose that all trajectories initiate from the site of electron attachment (the nitrogen atom). For each series, we use the calculated π orbital spin populations to distinguish the ortho, meta, and para sites and then, for comparison, we use values normalized with respect to the value calculated for the para site (see Figure 1). The "trap" itself is positioned on the chlorine atom in the three-dimensional reaction space, Figure 2.

Our results for $\langle n \rangle$ and the experimental results of Neta and Behar[1] are given in Table I. Since various statistical assumptions can be made on the proportionality between $\langle n \rangle$ and τ, we bypass this question by reporting values of $\langle n \rangle^{-1}$ (proportional to the first-order rate constant) normalized with respect to the value of $\langle n \rangle^{-1}$ calculated for the para site. A corresponding normalization is constructed for the experimentally determined rate constants and from Table I it is seen that the experimental and theoretical values (column 3 vs. columns 6 and 9) are in reasonable agreement whether one uses the actual or normalized π orbital spin populations. We remark that the π orbital spin population calculated for the meta position is so small that it is extremely sensitive to the type of MO calculation performed. In fact the INDO calculation yields a negative π orbital spin population at the meta site;[5] our calculation of τ for this case was carried out by using an effective trap depth of 0.00001, and the values of $\langle n \rangle_{\text{meta}}^{-1}/\langle n \rangle_{\text{para}}^{-1}$ reported here represent upper bounds. The best agreement between theory and experiment is achieved when the rate ratios are calculated by assuming all trajectories are initiated from the site of initial electron attachment (see column 3 vs. 9 of series II in Table I).

In conclusion, what the above calculations demonstrate is the importance of considering *both* quantum *and* statistical factors in determining the first-order rate constants for electron transfer reactions in anion radical systems. On the basis of energetic considerations alone (viz., the quantum-chemical evidence presented in Figure 1), one would anticipate an ordering of rate constants of meta < ortho < para; this is *not* the ordering found experimentally. On the other hand, if one considers only steric effects (by assuming *identical* π orbital spin populations at the ortho, meta, and para positions), one finds that whether one assumes all trajectories are initiated from the site of electron attachment or whether one averages over all possible initial configurations, confining one's attention to the statistics alone leads to walk lengths $\langle n \rangle$ ordered as ortho < meta < para (see footnote 6) and hence rate constants ordered as para < meta < ortho; once again, this is *not* the ordering found experimentally. Only when one couples both the quantum and statistical features of the problem does one find qualitative (and near quantitative) agreement with the experimental results.

A quantum statistical version of the above theory will be presented subsequently along with extensive calculations and comparisons on the variety of anion radicals studied by Neta and co-workers.[1,7-10] The point of this letter is to demonstrate that, at the very least, ratios of first-order rate constants for this class of reactions can be calculated directly from molecular orbital theory in tandem with an exact lattice statistical theory to determine the lifetime of the electron before bond breakage.

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(5) The authors are grateful to Prof. R. H. Schuler for alerting us to the possibility that the meta position may be characterized by a negative π orbital spin population.

(6) For example, when the trap depths at the ortho, meta, and para positions are set at the same value (0.5), averaging over all possible initial configurations leads to the results $\langle n \rangle_{\text{ortho}} = 422.590$, $\langle n \rangle_{\text{meta}} = 472.685$, and $\langle n \rangle_{\text{para}} = 501.612$. If one assumes that all trajectories initiate from the site of electron attachment, the results for this case are $\langle n \rangle_{\text{ortho}} = 417.834$, $\langle n \rangle_{\text{meta}} = 506.216$, $\langle n \rangle_{\text{para}} = 546.168$.

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