the normal frequencies of branched alkanes as accurately as *n*-alkanes.

The relative populations of rotational isomers of *n*-hexane and *n*-heptane at 298.15 K were calculated from the ΔG's among these isomers obtained from the present force field and neglecting the intermolecular interactions.[17] The integrated intensities of normal modes for the rotational isomers whose populations were larger than 5% were calculated and the absorbance of the mixture at wavenumber ν, $A_m(\nu)$, were calculated by eq 22 where $A_k(\nu)$ and

$$A_m(\nu) = \sum_k p_k A_k(\nu) \qquad (22)$$

p_k are the absorbance and the population, respectively, of the kth isomer, the former being calculated by eq 16. The simulated spectra of *n*-hexane and *n*-heptane are compared with the observed spectra in the liquid state at room temperature in Figures 4 and 5, respectively, where the conformers contributing to the intensity of individual simulated bands are shown. The half-bandwidth for these simulated spectra was assumed to be 10 cm^{-1} from the observed value of the isolated band at 1140 cm^{-1} of *n*-hexane. When this half-width was used, the heights of the CH_2 rocking bands near 720 cm^{-1} agreed well with observed heights. The simulated band at 1140 cm^{-1} in the spectrum of *n*-hexane and those near 1300 cm^{-1} in both the spectra due to gauche conformers are too weak compared with the observed bands. The enthalpy differences among the rotamers of *n*-hexane calculated by the present potential agreed well with the observed values in the liquid state.[17] Therefore, these disagreements may be caused by the inadequacies of a part of intensity parameters for gauche conformers. According to a preliminary calculation, the underestimated intensities of the bands due to the gauche conformers can be enhanced by increasing the intrinsic atomic charge of the hydrogen in the C–C–C plane, which includes the gauche C–C bond, and by adding a negative charge flux on this hydrogen with respect to the ∠HCC bending coordinate. These modifications of the intensity parameters seem to be favorable also for fitting the spectra of cyclohexane and its deuteriated derivatives, but more extensive work is necessary for estimating their best values. In other respects, the simulated spectra explain the appearance of many bands assignable to different rotamers on the change of state.

The reproduction of the thermodynamic functions and the structure parameters of alkanes and the success of simulations of infrared spectra of *n*-alkanes show that the atomic charges and charge fluxes assumed in this work can be used simultaneously as the potential parameters and the infrared intensity parameters. Extention of this approach to more polar molecules is now in progress.

Acknowledgment. This work was supported by a Grant-in-Aid for Scientific Research (No. 62570964) from the Ministry of Education, Science and Culture. The calculation in this work was performed on FACOM M-780 and FACOM VP-200 computer systems in the Data Processing Center, Kyoto University.

Communications to the Editor

Reactivities of Ester Radical Anions

John Masnovi* and Jeanne Maticic

Department of Chemistry, Cleveland State University
Cleveland, Ohio 44115

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A common reaction of radical anions is decomposition to produce an anion and a radical fragment.[1-3] The rate of this process determines the efficiency of many reactions, such as electron-transfer quenching of excited states, in which the initial electron transfer is reversible.

Our interest in reactions that are driven by dissociative electron transfer[4-6] led us to examine the reduction of esters of carboxylic acids. Alkyl benzoates in 2% ethanolic 2-propanol quench the absorption of solvated electrons ($\lambda_{MAX} \sim 700$ nm[7]), generated by pulse radiolysis,[8] with rate constants $k_e = (5 \pm 1) \times 10^9$ M^{-1} s^{-1}. Two transient absorption bands, appearing at 310 nm ($\epsilon \sim$ 35 000 M^{-1} cm^{-1}) and 445 nm ($\epsilon \sim 9500$ M^{-1} cm^{-1}), form si-

Table I. Rates of Decomposition of Ester Radical Anions

substrate	k (s^{-1})[a] alcohol (λ_{MON})[b]	k (s^{-1})[a] hexane (λ_{MON})[b]
$CH_3OCOC_6H_5$	5×10^3 (310, 445)	4.1×10^4 (305, 440)
$CH_3CH_2OCOC_6H_5$	5×10^3 (310, 445)	4.1×10^4 (305, 440)
$C_6H_5CH_2OCOC_6H_5$	4.8×10^4 (310, 445)	2.2×10^5 (440)
$(C_6H_5)_2CHOCOC_6H_5$	4.6×10^5 (330,[d] 450)	5×10^6[c] (330,[d] 440)
C_6H_4-*o*-$(COOCH_2CH_3)_2$	$\leq 1 \times 10^3$[e] (340, 780)	$\sim 4 \times 10^4$[e] (330)
$C_6H_5COOCOC_6H_5$	[f]	3.2×10^5 (300, 450)
$C_6H_5CH_2OCOCH_3$	1.4×10^6 (310[d])	$\geq 2 \times 10^6$[c]
$(C_6H_5)_2CHOCOCH_3$	$>2 \times 10^6$[c] (330[d])	$\geq 5 \times 10^6$[c]

[a] Decay of radical anions at 22 ± 1 °C. [b] Monitoring wavelength(s), nm. [c] Rates greater than experimental resolution. [d] Growth of radical monitored (k or k'). [e] Decay nonexponential even at low OD. [f] Not determined.

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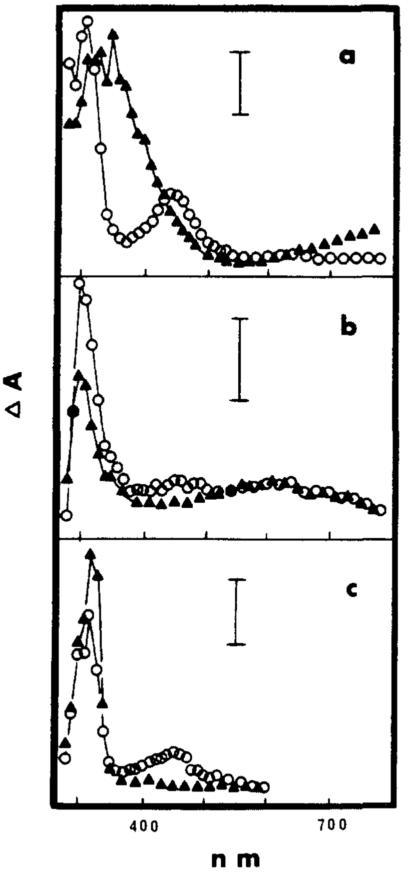


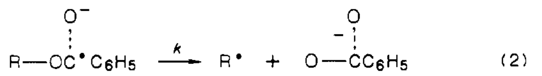
Figure 1. Difference transient absorption spectra (a) of ethyl benzoate (circles) and diethyl phthalate (triangles) in alcohol 1 μs after a 100-ns pulse of electrons, (b) of benzoic anhydride in hexane 0.4 μs (circles) and 3 μs (triangles) after pulse, and (c) of benzhydryl benzoate in alcohol 0.4 μs (circles) and 4 μs (triangles) after pulse. Bars indicate an absorbance of 0.02.

multaneously with the bleach of the 700-nm absorptions (Figure 1a). Both bands are quenched by oxygen at the same rate. Identical spectra are observed for all of the benzoates examined in Table I. The spectra are unaffected by the presence of 10 mM KOH. The absorptions resemble the spectrum of acetophenone ketyl anion.[12] Accordingly, we assign both bands to the solvated radical anions of the alkyl benzoates, $ROCOC_6H_5^{\bullet -}$, formed as described in eq 1.

$$ROCOC_6H_5 + e^- \xrightarrow{k_e} ROCOC_6H_5^{\bullet -} \qquad (1)$$

The absorptions derived from substituted benzoates, such as diethyl phthalate (Figure 1a), are quite different, however. This is consistent with delocalization of spin and charge density into the benzene rings of the radical anions which is affected by the substituent.[8]

The decays depend upon the alkyl group, R (Table I). Methyl benzoate and ethyl benzoate decay with essentially first-order rate constants $k \sim 5 \times 10^3$ s^{-1} at low dose.[13] The first-order rate constants increase in the order R = primary alkyl < benzyl < benzhydryl. Stabilization of an alkyl radical center ($R^\bullet$) increases in the same order. These trends suggest that the benzoate radical anions decay to afford benzoate and an alkyl radical (eq 2).[14] The major volatile products of these reactions have been identified as



$$R{-}O\overset{O^-}{\overset{\vdots}{C}}{}^{\bullet}C_6H_5 \xrightarrow{k} R^\bullet + O{-}\overset{O}{\overset{-\vdots}{C}}C_6H_5 \qquad (2)$$

those resulting from radical dimerization (~30% bibenzyl and ~40% 1-phenyl-2-propanol from benzyl radicals)[16] or reduction or disproportionation (alkanes and alkenes from secondary or tertiary alkyl radicals), in addition to quantitative yields of benzoic acid.[17] Reaction 2 formally involves homolysis of a C—OC(=O) bond. Stabilization of the radical site is expected to weaken this bond and facilitate cleavage.[18] Similar effects have been found to operate in the decays of radical anions of other benzylic derivatives, such as benzyl halides[2] and acetate.[3]

Benzyl radicals have absorption bands in the same region as the benzoate radical anions. The overlap of the absorptions of the benzoate radical anions with those of the more weakly absorbing benzyl radicals[10] obscures the formation of benzyl from the radical anion of benzyl benzoate; however, it is possible to observe clearly the benzyl radical in related cases. Diphenylmethyl benzoate initially affords the spectrum of the radical anion (Figure 1c). At longer times, the absorptions of the radical anion are replaced by those of the diphenylmethyl radical, which has an intense maximum at 330 nm ($\epsilon \sim 4 \times 10^4$ M^{-1} cm^{-1}).[11] The formation of the radical and the decay of the radical anion occur with the same first-order rate constant. The diphenylmethyl radical subsequently decays with second-order rate constant, 3×10^9 M^{-1} s^{-1}.[19,20]

Pulse radiolysis of alkyl benzoates in hexane produces radical anions which absorb near 305 and 440 nm. The absorptions are only slightly affected by the change in solvent. However, the rates of decay are considerably higher in hexane than in alcohol (Table I). These differences may reflect better stabilization of the radical anion by solvation in alcohol. The charge should be more localized in the anion radical than in the transition state, in which a carboxylate anion is partially formed (eq 2). Therefore, a polar protic solvent will result in a decrease in reaction rate compared to a nonpolar aprotic solvent.

Examination of the radical anion of benzoic anhydride proved interesting in the following respects. The absorptions of this radical anion were similar to those of benzoate ester anions. Furthermore, a fragmentation occurs to afford benzoyl radical (eq 2, R = C_6H_5CO), identifiable as a broad maximum near 650 nm[22] (Figure 1b). The rate of cleavage of the anhydride radical anion in hexane is similar to that for radical anion of benzyl benzoate, and it is significantly faster than the rates of cleavage of alkyl benzoates. This result confirms that benzoate ester radical anions do not afford appreciable amounts of acyl radical, and it indicates that

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(20) Flash photolysis of esters in the presence of amines affords similar results. However, additional absorptions at 650–680 nm appear in the flash photolysis experiments. The behavior of these absorptions in the presence of KOH or of amines which form acidic radical cations[21] suggests the 650-nm absorptions may be due to protonated radical anions. These results will be reported separately.

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acyl radical is about as good a leaving group as are benzyl radicals under these conditions.

The behavior of acetate esters also was examined briefly. Acetates quench the absorptions of the solvated electrons with rate constants $k_e' = (2 \pm 0.5) \times 10^9$ M^{-1} s^{-1} in alcohol. Pulse radiolysis of benzyl acetate afforded benzyl radical as the only transient detected optically above 300 nm. The growth of the benzyl absorption was slower than quenching of the solvated electrons and is taken to represent k', the rate of fragmentation of the acetate radical anion (Table I). Thus, the fragmentation of benzyl acetate anion is 30 times faster than that of benzyl benzoate anion. Other considerations, including solvation, spin and charge delocalization, polarizabilities, and steric effects, also are expected to affect the rates of cleavage.[16]

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Configuration-Dependent Photoisomerization of (*E*)-Cinnamamides

Frederick D. Lewis,* Jeffrey E. Elbert, Alana L. Upthagrove, and Paul D. Hale

Department of Chemistry, Northwestern University
Evanston, Illinois 60208

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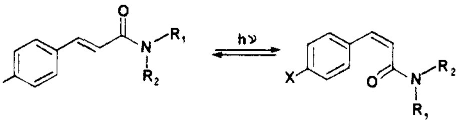
The reactivity of electronically excited molecules is dependent upon the configuration and multiplicity of the excited state.[1] A well-known example of configuration dependence is the Norrish type II reaction of aryl alkyl ketones, which occurs via the $^3n,\pi^*$ but not the $3\pi,\pi^*$ state.[2] Aromatic substituents can alter the energies of these states and thereby affect the reactivity. We have observed that the *E*,*Z*-photoisomerization efficiencies of a series of (*E*)-cinnamamides are highly dependent upon both N-alkylation and aromatic substitution (eq 1). These results are attributed to the existence of two low-energy $^1\pi,\pi^*$ states, a reactive state with a styrene-like HOMO, and an unreactive state with an amide nonbonding π HOMO. The energy of the former state can be altered by aromatic substituents, while that of the later state can be altered by N-alkylation. This is, to our knowledge, the first instance in which the energies of two states of the same multiplicity can be independently varied via substitution at two different sites in the molecule.



(1)

1: $R_1 = R_2 = H$
2: $R_1 = CH_3$; $R_2 = H$
3: $R_1 = R_2 = CH_3$

While the photoisomerization of (*E*)-cinnamamides has been reported as a method for preparing the (*Z*)-isomers,[3] this process has eluded the mechanistic scrutiny to which cinnamic acid and its esters have been subjected.[4] Absorption spectral data and isomerization quantum yields (Φ_i) obtained from 313 irradiation of 0.01 M dichloromethane solutions of several (*E*)-cinnamamides are summarized in Table I. IR and NMR spectral analyses confirm that the ground states of all of the (*E*)-amides adopt a planar s-trans conformation in solution as in the solid state[5] and are predominantly in monomeric form at the concentrations used in the spectroscopic and photochemical investigations. The marked dependence of Φ_i upon N-alkylation and aromatic substitution stands in contrast to reported results for cinnamic acid and several of its ring-substituted esters, all of which isomerize with $\Phi_i > 0.20$.[4a] Triplet-sensitized irradiations of **3a** or **3b** (0.01 M Michler's ketone, 365 nm) occur with $\Phi_i = 0.55$ and 0.53, respectively, whereas attempted triplet quenching with 1,3-pentadiene (0.2–2.0 M) did not alter Φ_i. Thus we conclude that intersystem crossing is inefficient for the cinnamamides and that the Φ_i values in Table I are determined by partitioning of the nonfluorescent singlet state(s) between isomerization and nonradiative decay.

The effect of N-alkylation upon the electronic structure of the cinnamamides was investigated with Gaussian 82 calculations.[6] The frontier orbitals include a styrene-like HOMO (π_S) and LUMO (π^*) for **1a**–**3a**, similar to those previously reported for methyl cinnamate.[4b] In addition, there are the two high lying orbitals observed by Turner and co-workers[7] for the amides of formic and acetic acid: the carbonyl oxygen lone pair (n_O) and the approximately nonbonding antisymmetric π_N. The nodal properties and approximate atomic coefficients of the π orbitals are shown in Chart I and the orbital energies summarized in Table II. While the energies of the n_O, π_S, and π^* orbitals are relatively insensitive to N-alkylation, the energy of π_N is seen to increase with N-alkylation, as previously observed for simple amides.[7] The π_S orbital lies well above π_N or n_O in cinnamamide (**1a**), whereas in acrylamide the π(C=C) orbital lies below n_O and π_N.[8]

The presence of two high-lying π-orbitals should result in two singlet states (π_S,π^* and π_N,π^*), which should not mix significantly due to the lack of overlap between the π_N and π_S orbitals. The π_S,π^* state would be expected to isomerize efficiently, as it does in the case of the cinnamic esters,[4a] whereas the π_N,π^* state retains a higher C=C bond order and thus should resist isomerization. The effects of aromatic substituents on λ_{max} (Table I) support the assignment of the UV absorption band to a $\pi^* \leftarrow \pi_S$ transition. The $\pi^* \leftarrow \pi_N$ transition is not resolved but may be responsible for long-wavelength tails and shoulders.

While the relative energies of the π_S,π^* and π_N,π^* states will depend upon the extent of configuration interaction, we assume as our working hypothesis that the lowest singlet of **1a** is the reactive π_S,π^* and the lowest singlet of **3a** is the unreactive π_N,π^* state. This hypothesis provides a conceptually simple framework for understanding the consequences of N-alkylation and aromatic substitution. N-Alkylation should lower the energy of the π_N,π^* state but have little effect on the energy of the π_S,π^* state (Table II). The electron-donating methoxy group should raise the π_S energy and thus lower the energy of the π_S,π^* singlet state (but not π_N,π^*). A large red shift in the long-wavelength absorption band of **1b** vs **1a** and **3b** vs **3a** and a dramatic increase in Φ_i, especially in the case of **3b** vs **3a**, are, in fact, observed. Conversely, the electron-withdrawing trifluoromethyl group should lower the π_S energy and thereby raise the energy of the π_S,π^* state. The blue-shifted absorption bands of **1c** vs **1a** and **3c** vs **3a** and the decrease in Φ_i for **1c** vs **1a** conform to this prediction. Raising the π_S,π^* energy should have no effect on Φ_i in the case of **3c** vs **3a**, if the lowest singlet is π_N,π^* in both cases.

Additional support for the two singlet hypothesis comes from the effect of BF$_3$ complexation upon Φ_i. All of the amides form stable BF$_3$ complexes ($K > 1000$) with red-shifted absorption compared to the free amide and all of the Lewis acid complexes have $\Phi_i \geq 0.35$ ($\Phi_i = 0.55$ for **3a**:BF$_3$). Gaussian 82 calculations

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