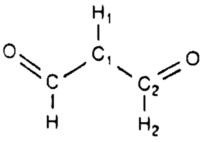

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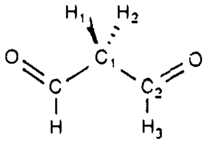

65 (Cs)

and −0.59 kcal/mol. The value of the ΔRSE indicates the presence of slight destabilization in **64** relative to twice the RSE for the formylmethyl radical.

In this final series of cyano- and formyl-substituted methyl radicals there is no indication of a significant destabilization being present in the dicaptor-substituted radicals, even in the very highly electronegatively substituted diformylmethyl radical.

Summary of the Pentadienyl-Type Delocalized Radicals. The calculated ΔRSE's of the pentadienyl-type, five-electron delocalized radicals mostly indicate that these systems possess slight extra stabilization relative to the sum of the stabilizations present in the singly substituted methyl radicals, even in systems containing two relatively strong electron-withdrawing functions. This is not consistent with the captodative concept, which would have predicted net destabilization in such systems.

A simple MO analysis provides some insight as to why this is so. In the pentadienyl-type systems, the bonding MO's Ψ_1 and Ψ_2 are doubly occupied, with the SOMO being the nonbonding pentadienyl MO Ψ_3. In this case it is not necessary to occupy an antibonding MO as in the case of the butadiene-type, five-electron radicals. A further stabilization is gained by the decreased π-space electron repulsion in the pentadienyl-type systems compared to the butadiene-type systems.

Summary

The results of the present calculations indicate that substantial captodative stabilization is present only in the allyl-type, three-electron radicals **9**, **11**, and **13**. The results of the calculations on the butadiene-type, five-electron, donor–acceptor substituted radicals **36**, **38**, and **42** predict weak net *destabilization*, while the results on **40**, **44**, and **46** predict weak net *stabilization*. *There is no evidence for the existence of a significant captodative stabilization in these donor–acceptor substituted radicals.* The stabilization and destabilization effects are very sensitive to the relative electronegativity of the substituents attached to the radical centers. The calculations on the pentadienyl-type, five-electron radicals indicate the presence of slight to moderate extra stabilization not anticipated by the captodative concept, except for the highly electronegatively substituted radicals **62** and **64**. The trends in the ΔRSE's have been discussed in terms of the type of MO's and their occupancy and the relative electronegativity of the attached substituents.

The present results suggest that the results of many studies that have been interpreted in terms of supporting the captodative concept may need to be reevaluated, in particular those reactions that involve radical formation by radical additions to substituted alkenes and allenes. In such radical addition reactions the transition states are expected to occur early along the reaction coordinates in which reactant ground state electronic properties are expected to control reactivity, and not substituent effects on the developing radical center.

In the isomerization reactions of the substituted allyl radicals discussed in the introduction, the present calculations indicate that the observed trend in energy barriers cannot be explained on the basis of a captodative stabilization in the transition state for the isomerization of the 1-cyano-1-methoxyallyl radical. In this isomerization reaction ground state destabilization must be the major contributing factor causing the lowering of the energy barrier for isomerization. Further theoretical studies will be devoted to analyzing these effects.

In view of the general conclusions arrived at in this article, it is instructive to inquire as to why the approach to the captodative effect based on resonance theory is not universally valid. This would appear to be due to the fact that it was only the *number* of resonance contributing structures that was considered in the analysis of the substituted radicals, and not their relative importance. If all of the resonance structures considered contributed equally to the resonance hybrid, then the analysis would have been correct. In fact, consideration of the charge separations in some of the contributing structures to **3** would indicate that some structures would contribute to a much smaller extent, thus flawing the approach.

Acknowledgment. This research was supported, in part, by a National Science Foundation Grant (CHE87-09725).

Supplementary Material Available: Tables of the calculated geometrical parameters for the mono- and disubstituted methyl radicals and methanes (46 pages). Ordering information is given on any current masthead page.

Influencing Reactivity by Monolayer Compression: An Alcohol Dehydration

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Abstract: The kinetics of the acid-catalyzed dehydration of 1,1-diphenyl-1-octadecanol have been examined at the air–liquid interface. The rate of reaction was found to be strongly dependent on the area/molecule in the monolayer. For expanded films with large areas/molecule the rate of dehydration was over 20 times that for compressed films. The results have been interpreted in terms of the availability of the β-hydrogens to the acid subphase. With highly expanded films the hydrophobic chains are deduced to be essentially independent, affording facile access of the subphase to the β-hydrogen. For compressed films and those of intermediate areas/molecule the hydrophobic chains are interacting and the β-hydrogens are oriented away from the subphase. A threshold value of the area/molecule for β-hydrogen access has been determined.

Reactions in monolayer assemblies provide the opportunity to examine the reactivity of molecules constrained in a plane. The geometrical requirements of transition states may be inferred from the reactivity of the films at varying areas/molecule allowed to the monolayer; e.g., the acid-catalyzed cyclization of the monoterpenoid alcohol nerol is strongly disfavored at low areas/mol-

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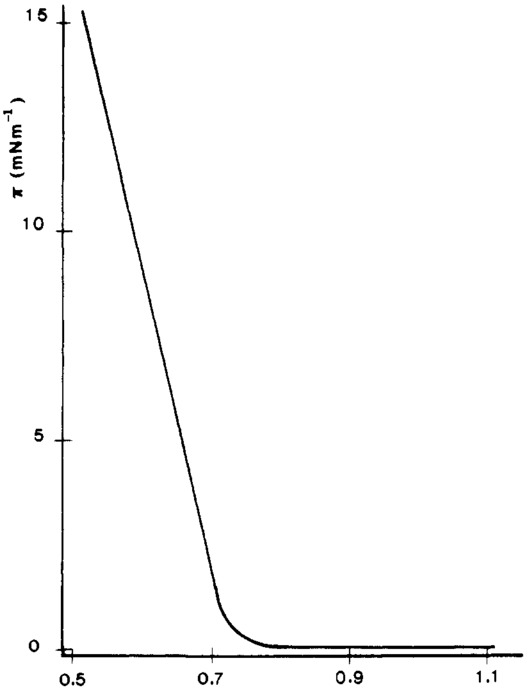
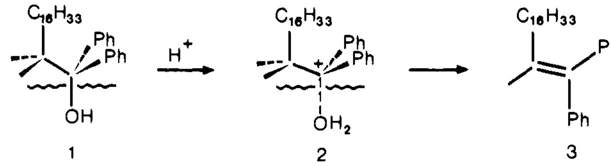


Figure 1. Π–*A* isotherm at 25 °C using Wilhelmy balance (initial film area 170 cm^2, final area 80 cm^2, compression rate 24 cm^2 min^{-1}).

ecule, i.e., high surface pressures, since the coiled conformations required for cyclization cannot be accommodated.[1] However, at large areas/molecule the remote double bond can access the reaction site and cyclization occurs readily. By contrast, the kinetics of the chromic acid oxidation of 1-phenyl-1-hexadecanol to 1-phenyl-1-hexadecanone[2] and of the hydrolysis of an octadecyl ester[3] are not greatly influenced by surface pressure changes. In both these examples reaction is taking place at a single carbon atom, and the geometry of the hydrophobic chain may be expected to have only a small effect on the rate of reaction.

To explore further the generality of these novel effects, the acid-catalyzed dehydration of 1,1-diphenyl-1-octadecanol (**1**) to 1,1-diphenyl-1-octadecene (**3**) has been investigated at the air–liquid interface to assess the role of the hydrophobic chain at differing areas/molecule.



Results and Discussion

A clear prerequisite for the effective study of the kinetics of reactions in monolayer assemblies is the ability of the substrate to form films stable within the time frame of the experiment. The monolayer film of 1,1-diphenyl-1-octadecanol does indeed satisfy this requirement. The surface pressure–area (Π–*A*) isotherm (Figure 1) is entirely typical of amphipathic systems; the limiting area (obtained by extrapolating the Π–*A* isotherm to zero Π) of ca. 0.72 nm^2 is larger than for simple alkyl chains such as stearic acid, where the limiting area is 0.21 nm^2,[5] because of the two phenyl groups inhibiting further compression. Leaving a compressed film of the alcohol, Π = 15.0 mN m^{-1} over water for 40 min produced a <10% decrease in Π, pointing to considerable film stability. The alkene product **3** was found not to be surface active.

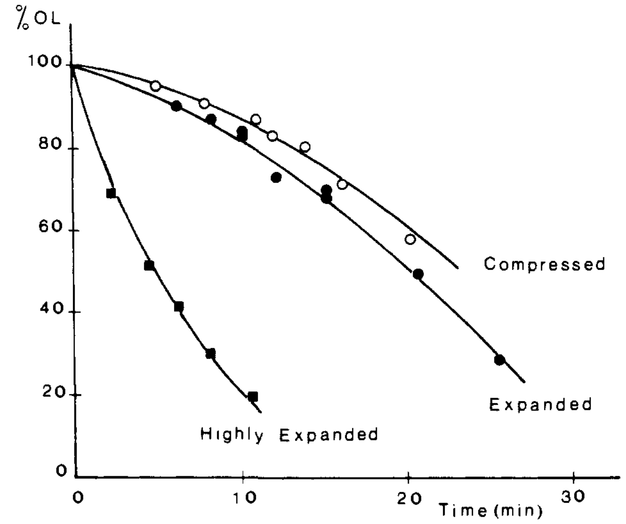


Figure 2. 1,1-Diphenyl-1-octadecanol (OL) concentration versus reaction time for "highly expanded", "expanded", and "compressed" films over 44% sulfuric acid at 25.0 ± 0.1 °C.

Table I. Pseudo-First-Order Rate Constants for Dehydration on 44% Sulfuric Acid at 25.0 ± 0.1 °C

film type	(area/molecule)/nm^2	k/s^{-1}
compressed	0.57	$(1.1 \pm 0.1) \times 10^{-4}$[a]
expanded	1.7	$(1.2 \pm 0.2) \times 10^{-4}$[a]
highly expanded	8.0	$(2.52 \pm 0.08) \times 10^{-3}$

[a] Derived by fitting concentration plot up to 1 half-life to a cubic and differentiating to give initial rate; see, e.g., ref 6b.

The kinetics of the alcohol dehydration were followed by HPLC analysis of reaction mixtures derived from monolayer films reacted for appropriate reaction times.

The experiments were performed on a modified Langmuir trough consisting of a thermostated multicompartment PTFE trough with a Wilhelmy plate balance.[4] The subphases, water and 44% or 48% sulfuric acid, could be confined to different compartments, and the monolayer could be transferred from one to the other by coupled motion of the confining barriers with minimal mixing of the subphase material.

Considerable care in cleaning the apparatus between runs is required to give reproducible data. Before each run the trough was washed with concentrated sulfuric acid and copious quantities of water.

Three film types were examined in detail, namely, "highly expanded", "expanded", and "compressed". The expanded and compressed films were formed by spreading 3 and 10 μL of a 2.6 × 10^{-3} M solution of the alcohol in hexane on water and reducing the available surface area to 1.7 and 0.57 nm^2/molecule, respectively. The corresponding surface pressure values were <0.1 and 15 mN m^{-1}, respectively.

The highly expanded film was prepared by spreading 1 μL of the alcohol solution on an area that gave a film of 8.0 nm^2/molecule, i.e., 4.7 and 14 times as large as the areas/molecule of the normal expanded and compressed films, respectively.

Once formed, the films were transferred to the sulfuric acid subphase contained in adjacent compartments of the trough at 25 °C. After a given time at constant area, the monolayer was swept into a reservoir in the trough containing hexane, where the reaction mixture dissolved. Typical recoveries were >90%, and the alkene **3** was found to be unreactive, <1%, at the longest reaction times studied.

Despite the low quantities of alcohol and alkene in the reaction mixture of ca. 10^{-5} g, they could be readily analyzed by HPLC, using Lichrosorb RP8 10-μm column. Both **1** and **3** are detected in the UV at 210 nm at 0.02 absorbance unit full scale (AUFS); the peaks were integrated electronically, and concentration was

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calculated by using the molar response factors calculated from a standard solution of **1** and **3**.

The surface reaction kinetics may be described as pseudo first order (Figure 2). The dramatic rate enhancement for the highly expanded film is apparent from the plot. The increasing rate of compressed and expanded films with time reflects the change in film character; as the product alkene is formed and desorbed from the surface, more space is available for the alcohol molecules, and the rate increases accordingly. The rate constants quoted in Table I for these film types are those derived from initial rates.[6a]

Reaction of a highly expanded film (7.7 nm^2/molecule) over 48% sulfuric acid afforded a pseudo-first-order rate constant of $(5.04 \pm 0.43) \times 10^{-3}$ s^{-1} at 25 °C. Taking the difference in acidity function, H_0, for 44% and 48% sulfuric acid as −0.35,[9] this corresponds to a slope for log k against $-H_0$ of 0.86, indicating that the reaction is sharply acid catalyzed. The slope is within the range observed for dehydrations proceeding via cationic intermediates[8] and points to the similarities between bulk phase and surface reactions; indeed for the surface oxidation of 1-phenyl-1-hexadecanol by chromic acid, the pseudo-first-order rate constant is within 20% of that for the bulk phase oxidation of 1-phenylethanol using an identical oxidant.[2]

The rate ratio of highly expanded to compressed films of 23 is most readily understood in terms of the availability of the β-hydrogens of the substrate. In the compressed film the hydrophobic alkyl chains are oriented away from the acid subphase, and thereby precluded from participation. Such reaction that does occur presumably reflects imperfections in the compressed films.

In highly expanded films the alkyl chains are surmised to be lying on the surface, and the β-hydrogens are thus accessible to the subphase. The observation of this effect indicates the involvement of the β-hydrogen in the rate-determining step, a result consonant with kinetic isotope effect data obtained with similar systems.[7] An alternative explanation of the rate difference involves differing rates of return from the ion–molecular pair (**2**) to the protonated alcohol. Ion-pair return is ubiquitous in solvolysis chemistry, and the observation of large ratios of racemization to dehydration rate for 1-phenylethanol of >100 and 1,2-diphenylethanol of >60[7,10] points to the intermediacy of ion–molecule pairs or possibly free cations. However, we do not favor this explanation of the rate difference between highly expanded and compressed films, since the variation of available area/molecule appears to have a negligible influence on reactions taking place at a single center.[2,3] We would therefore not expect any significant variation in the rate of the return process of **2** to the protonated alcohol as the area/molecule increases.

The low reactivity of the expanded film is perhaps more surprising; the area/molecule is ~3 times that of the compressed film, yet the rate differs by only ~10%. At such areas the β-hydrogens should have facile access to the subphase. However, although space is available, the hydrophobic chains may still be interacting, forcing the β-hydrogens away from the subphase. This implies that the film is of the liquid type, i.e., coherent with cooperative interaction. Thus, although Π is <0.1 mN m^{-1}, the hydrophobic chains are oriented away from the subphase; indeed liquid type films may exist at Π values as low as 0.001 mN m^{-1}.[5]

It is tempting, therefore, to invoke a threshold area/molecule at which the monolayer forms a gaseous type film,[5] i.e., when the molecules are sufficiently independent to be able to acquire the syn-periplanar arrangement of the ion–molecular pair (**2a**) required for elimination on the surface.

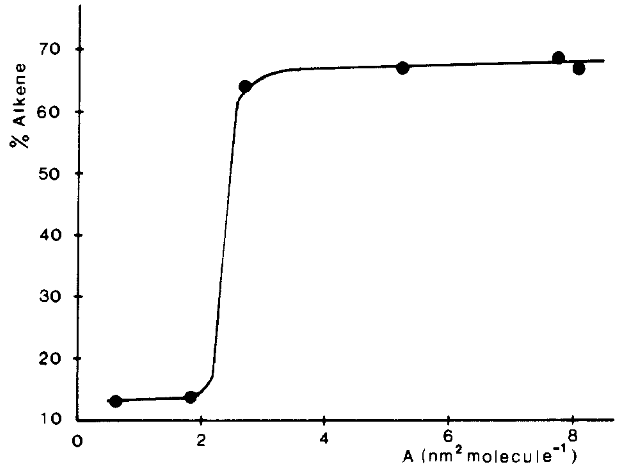
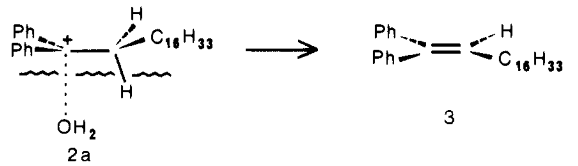


Figure 3. Percent 1,1-diphenyl-1-octadecene versus area/molecule for reaction over 48% sulfuric acid at 25.0 ± 0.1 °C and constant reaction time of 4 min (see ref 11).



In order to test this hypothesis, the reactivity of the alcohol film at several areas/molecule was determined over 48% sulfuric acid (Figure 3). The plot clearly shows a threshold area/molecule of ca. 2.5 nm^2 for the observation of an enhanced reaction rate. Above this value the reaction rate remains constant, all restraints to reaction having been removed. This threshold area/molecule may also be considered as diagnostic of the transition between liquid and gaseous film types.

Conclusions

The present investigation has demonstrated the dramatic effect that surface pressure (or area/molecule) variation can have on reactions involving part of the hydrophobic chain in reactions of monolayer assemblies. Reactions occurring at a single center show negligible effects, but functionalities as seemingly proximate as a β-hydrogen are seen to be able to access the subphase only at considerable areas/molecule.

This is best understood in terms of the transition from a liquid type to a gaseous type film. It appears that in liquid type films, despite the very low Π values, <0.1 mN m^{-1}, the hydrophobic chains are oriented away from the subphase with sufficient interaction to force the β-hydrogens away from the subphase. Only on formation of a gaseous type film, with independent hydrophobic chains, is facile access of the β-hydrogens permitted.

These studies suggest the availability of a novel tool for the investigation of neighboring group and proximity effects and therefore offer a new technique in the study of reaction mechanism.

Experimental Section

Materials. All water used was distilled through a Pyrex still and then doubly distilled with a Heraeus Destamat quartz still. Aqueous 44% and 48% sulfuric acid solutions were prepared by mass with Fluka (puriss) sulfuric acid.

1,1-Diphenyl-1-octadecanol was prepared by the Grignard reaction of phenylmagnesium bromide (80 mmol) with ethyl octadecanoate (TCI Chemicals, Tokyo >97% by GC) (37 mmol), affording the alcohol (22 mmol): 59% yield; mp 58–60 °C. Anal. Calcd for $C_{30}H_{46}O$: C, 85.25; H, 10.97. Found: C, 85.50; H, 10.99.

1,1-Diphenyl-1-octadecene was prepared by acid-catalyzed dehydration (50% H_2SO_4) of the alcohol **1** (2 mmol), affording the alkene (0.6 mmol): 33% yield; mp 34–36 °C. Anal. Calcd for $C_{30}H_{44}$: C, 89.04; H, 10.96. Found: C, 89.22; H, 11.05.

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(6) (a) The apparently simpler expedient of following the reactions at constant surface pressure was found to give erratic results, possibly arising from incipient film collapse as the area decreased. (b) Hall, K. J.; Quickenden, T. I.; Watts, D. W. *J. Chem. Educ.* **1976**, *53*, 493.

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(11) The curve in the region where the film undergoes the putative phase transition is too steep to allow precise measurements of the rate.

Equipment. For the reaction, a multicompartmental trough (manufactured by Mayer-Feintechnic, Gottingen), essentially a modified Langmuir trough, was used.[4] This trough is made from PTFE and is circular, 24-cm outside diameter, 12-cm inside diameter, and 0.3-cm depth. The height of the partitioning walls is just below that of the inner and outer walls of the trough, allowing continuity of liquid surface but preventing any appreciable intermixing of the liquid between compartments. The PTFE trough was clamped securely onto an aluminum base through which water could be circulated from a thermostated bath. Two PTFE barriers are connected through separate shafts to an axle. The barriers could be either moved independently, to vary the enclosed surface area, or moved in concert from one part of the trough to another with a fixed area enclosed. The decoupled motion was used to bring a spread surface film to a given surface pressure; the film could then be transferred to the sulfuric acid subphase in adjacent compartments with a coupled motion of the barriers.

Near one barrier was a glass-slide Wilhelmy plate connected to the core of a linear variable differential transformer where the output signal could be calibrated in terms of the surface tension acting on the glass plate. Surface pressure could be measured to 0.1 mN m^{-1} via a digital display. Π–A isotherms were recorded on a Hewlett-Packard 7045B X–Y recorder using analog output signals corresponding to surface pressure and area from the trough assembly.

One of the compartments had a deep rectangular well (6 cm × 1.5 cm × 4.5 cm deep), originally intended for the deposition of Langmuir–Blodgett films. It was found convenient to quench our reaction mixtures by sweeping them into this reservoir containing water and 1 mL of hexane. The hexane layer was then removed by Pasteur pipet for analysis by high-performance liquid chromatography (HPLC).

HPLC analyses were performed with an LKB system, with a LKB 2151 variable-wavelength monitor and an LKB 2220 recording integrator.

Kinetics. In a typical run, the two barriers were positioned with three compartments (120 cm^2, digital display) between them, containing a measured amount of triply distilled water. The compression barrier was used to sweep and compress any surface impurity, which was then removed from the surface by suction. The compression barrier was then withdrawn, and a suitable quantity of the hexane solution of the alcohol (2.6×10^{-3} M) was added with a Hamilton microliter syringe. The solution was seen to spread, and after 1 min the compression barrier was moved to adjust the enclosed surface area to the desired area/molecule.

The film was then transferred over to a measured amount of the reaction subphase by coupled motion of the barriers. To minimize mixing of the water and the reaction subphase (aqueous sulfuric acid), the film was swept over an intermediate "buffer" compartment containing the acid subphase before being brought over the reaction compartments.

After reaction of the film for a given time, the reaction mixture was swept into the reservoir in the trough containing 1 mL of hexane and water by coupled motion of the barriers. The hexane solution was withdrawn using a Pasteur pipet and analyzed by HPLC.

The reaction mixture could be readily resolved by isocratic elution with 70% 2-propanol–30% water on a 25-cm LKB RP8 10-μm column. Both the alcohol **1** and the alkene **3** were detected in the UV at 210 nm, and the peak areas were measured electronically. Repeat injections of the same sample were reproducible within 2%.

Each point in Figure 2 represents a complete kinetic run, from spreading of the alcohol **1** to the analysis of product by HPLC. Thus the standard errors in the rate constants k given in Table I reflect the reproducibility of the measurement from run to run. In addition to the comparison of the value of k calculated for each run, reproducibility was also checked for the same reaction times in each of the three film types. Duplicates of measurements carried out for each of the three film types for two reaction times selected randomly showed that the error was better than ±5%. However, to ensure reproducible results it was imperative that the trough was meticulously cleaned between runs, first with concentrated sulfuric acid and then with copious quantities of water. Blank runs revealed no residual products from previous runs with this method.

To assess the efficiency of the trough operations, an absolute recovery experiment was performed by spreading an amount of the alcohol **1** on water and sweeping it into the reservoir containing 1 mL of hexane. HPLC analysis of the hexane solution showed that the alcohol recovered was 93% of the material spread originally. In addition to measuring the percentage of the spread alcohol that was recoverable, the mass balance was determined for reaction by comparing the peak areas, corrected for differing response of alcohol **1** and alkene **3** at various reaction times. In all cases (mol of unreacted alcohol **1**) + (mol of alkene product **3**) > 0.9(mol of starting material **1**).

The reactivity of the alkene product **3** under the reaction conditions employed in the study was determined by spreading a hexane solution of the alkene on 44% H_2SO_4. After 30 min the surface material was swept into the reservoir containing hexane. No trace of the alcohol **1** was found by HPLC analysis, indicating the absence of hydration under these conditions. This is an entirely expected result since the alkene does not form a monolayer.

By comparison with our previous work on the acid-catalyzed nerol cyclization, the current methodology represents a considerable enhancement. Owing to the relative instability of nerol and geraniol films (solubility and evaporation problems), the results obtained by GLC analysis of reaction products are only qualitative. Recoveries were not determined, but were assumed to be low and at best variable. However, the reaction times were maintained strictly constant and the relative reactivities of the film types were accurately determined.

Properties of Anions, Radicals, and Radical Cations Derived from 9-(Dialkylamino)fluorenes

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Abstract: Equilibrium acidities for seven 9-(dialkylamino)fluorenes together with their oxidation potentials and those of their conjugate bases have been measured in Me_2SO solution. These data are used to estimate (a) the homolytic bond dissociation energies (BDEs) of the 9-C–H bonds in these molecules, (b) the acidities of the corresponding radical cations, and (c) the relative stabilities of the radicals formed on deprotonation of their radical cations. Comparisons are made with similar estimates of the effects of 9-(1-imidazolyl), 9-(3-methyl-1-pyrazolyl), 2-Me_2N, and 2,7-$(Me_2N)_2$ groups. The 2-Me_2N and 2,7-$(Me_2N)_2$ groups decrease the acidity of the fluorene radical cation by 18 and 24 kcal/mol, respectively, but have little effect on the BDEs of the 9-C–H bonds. On the other hand, the 9-dialkylamino groups were found to lower the BDEs of the 9-C–H bonds by 5–12.8 kcal/mol relative to that of fluorene (79.5) and to decrease the acidity of the fluorene radical cation by an average of only 6.5 $pK_{HA^{\cdot +}}$ units. The latter decreases are the net result of making both $E_{ox}(HA)$ more negative (acid weakening) and $E_{ox}(A^-)$ more negative (acid strengthening). By contrast, the 9-imidazolyl group weakens the 9-C–H bond by only 3.3 kcal/mol and increases the acidity of the corresponding radical cation by 3.6 $pK_{HA^{\cdot +}}$ units, relative to that of fluorene. The Me_3N^+ moiety of 9-Me_3NFlH^+ increases the 9-C–H BDE by 5 kcal/mol.

The anion derived from 9-(dimethylamino)fluorene is only 0.14 kcal/mol less basic than the fluorenide ion, but has an oxidation potential, $E_{1/2}(A^-)$, that is about 8 kcal/mol more negative. This difference can be equated to an 8 kcal/mol weakening by the Me_2N moiety of the homolytic bond dissociation energy (BDE) of the 9-C–H bond in 9-Me_2NFlH, relative to that in HFlH, or to an 8 kcal/mol stabilization of the 9-$Me_2NFl^{\cdot}$ radical, relative to the $HFl^{\cdot}$ radical.[1] Similar large effects of α-R_2N groups on

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