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H. Sakurai,* Y. Kamiyama, Y. Nakadaira

Department of Chemistry, Faculty of Science
Tohoku University
*Sendai 980, Japan*

Salem Diagrams as a Device for the Elucidation of Photochemical Reaction Mechanisms. Application to the Cleavage of Cyclic Alkanones

Sir:

The photochemical behavior of cyclobutanones contrasts sharply with that of higher cyclanones[1] (e.g., cyclohexanone). The main differences between the photoreactivities of cyclobutanone, **1**, and cyclohexanone, **2**, in condensed phases are as follows: (1) **1** undergoes α-cleavage from both the singlet and triplet n,π* excited states[2] whereas **2** cleaves exclusively from the triplet state.[3] (2) The singlet n,π* of **1** yields fragmentation (ketene and olefin, eq 1) cyclization (oxacarbene, eq 2) or decarbonylation (cyclopropane and CO, eq 3) products.[4] The parent triplet exclusively loses CO to form cyclopropane, presumably via trimethylene (eq 3), whereas the triplet of **2** undergoes disproportionation reactions (eq 4).[5] (3) The photochemical activity of **1** persists even at very low temperatures where **2** is photostable.[6]

$$CH_2{=}CH_2 + CH_2{=}C{=}O \qquad (1)$$

trapping products (2)

$^3n\pi^*$ → △ + CO (3)

(4)
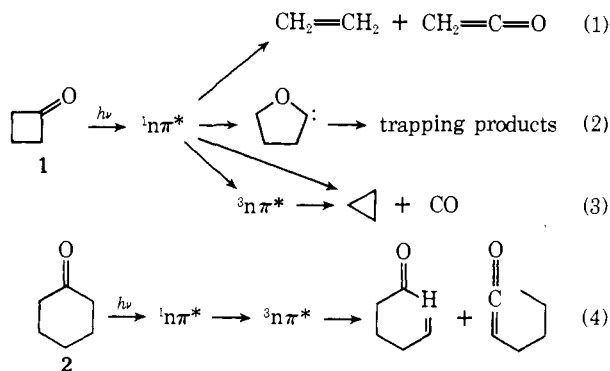
An elegant rationalization of the nature of the major products found in the photochemistry of alkanones is based on the postulate of homolytic type I α-cleavage (eq 5).[7] This postulate,

(5)
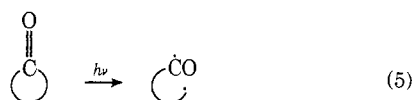
in combination with the concept of "ring strain" is usually invoked to explain the antithetic behaviors of **1** and **2**—in particular, points 1 and 3 above—but the question arises as to how the "memory" of strain release can persist after the cyclobutanone ring is cleaved and the 1,4 diradical formed. To
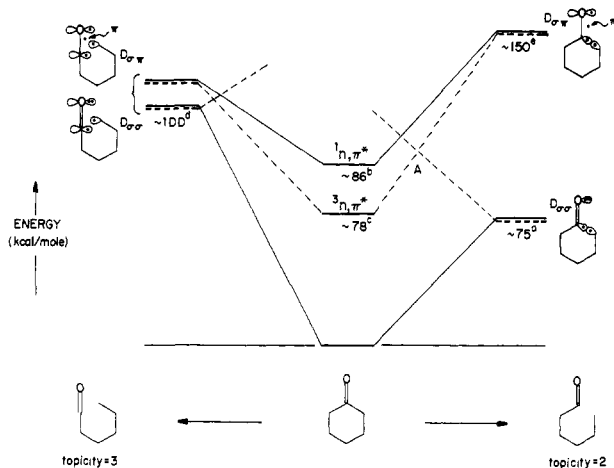
Figure 1. Comparison of α-cleavage of cyclohexanone to produce bent (reaction to the right) and linear (reaction to the left) acyl fragments. Dots indicate electron in various orbitals. All electrons indicated have σ-symmetry with respect to the molecular plane except for the π electrons which are explicitly indicated in the figure: (a) group additivity, ref 13a; (b) ref 4 (for cyclopentanone); (c) ref 3a, ref 4 (for cyclopentanone); (d) ΔH_f bent diradical + calculated linearization energy ref 8b (acetyl), ref 15 (formyl); (e) ref 8b (for acetone). The cleavage to form a bent acyl radical, although formally tritopic, is more realistically treated as ditopic because of the large energy gap between the $D_{\sigma,\sigma}$ and $D_{\sigma,\pi}$ states at the diradical geometry.
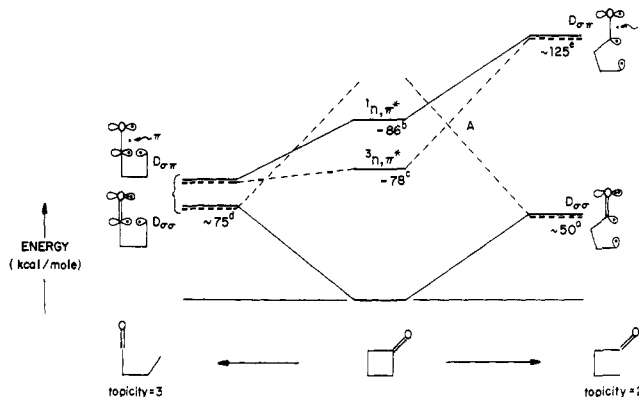
Figure 2. Comparison of α-cleavage of cyclobutanone to produce bent (reaction to the right) and linear (reaction to the left) acyl fragments. Dots indicate electron in various orbitals. All electrons indicated have σ symmetry with respect to the molecular plane except for the π electrons which are explicitly indicated in the figure: (a) group additivity; (b) ref 2; (c) ref 4; (d) ΔH_f bent diradical + calculated linearization energy ref 8b (acetyl), ref 15 (formyl); (e) ref 8b (for acetone). The cleavage to form a bent acyl radical, although formally tritopic, is more realistically treated as ditopic because of the large energy gap between the $D_{\sigma,\sigma}$ and $D_{\sigma,\pi}$ states at the diradical geometry.

probe this question Salem theoretical diagrams[8] for the coplanar α-cleavage of **2** (Figure 1) and **1** (Figure 2) were combined with available thermochemical and spectroscopic data on these systems. These diagrams use distinct reaction coordinates to depict two major types of coplanar α-cleavages. On the right hand side the CO···C bond is stretched while maintaining a bent acyl moiety. The left hand side represents the elongation of the CO···C linkage with concomitant linearization of the acyl fragment. Let us note that both processes are formally [σ,(σ,π)] tritopic.[8] Still the energy gap between the σ and π radical sites of the bent acyl is large enough (σ below π) for the $D_{\sigma\pi}$ singlet and triplet pair of diradical states to be much higher in energy than the parent $D_{\sigma\sigma}$ pair.[9] The manifold of states associated with the cleavage to a bent acyl fragment is somewhat reminiscent of the simpler bitopic pattern.[8]

Figure 1 reveals that both cyclohexanone cleavages—with retention of the bent geometry or with linearization—are
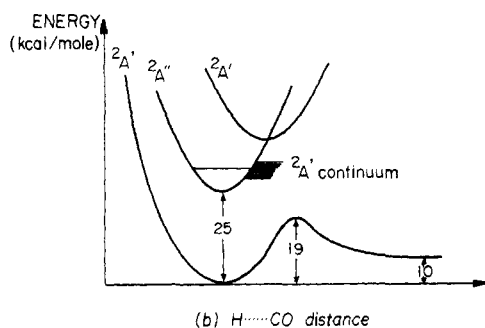
Figure 3. Variation of HCO electronic states with increasing H···CO distance. The ground state activation energy of 19 kcal for the formyl radical is the recommended value of Benson and O'Neal. (S. W. Benson and H. E. O'Neal, "Kinetic Data on Gas Phase Unimolecular Reactions", NSRDS-NBS 21, U.S. Dept. of Commerce, Washington, D.C., 1970).

photochemically forbidden. The former (bent geometry) is *thermochemically feasible* (the singlet and triplet n,π* states of **2** and the ground state, $D_{\sigma\sigma}$, of the bent diradical have roughly similar energies) but might be viewed as *electronically forbidden* since the ^{1,3}n,π* states correlate with high-lying $^{1,3}D_{\sigma,\pi}$ functions.[9] The latter (linearization) is *electronically allowed* due to the stabilization of the $^{1,3}D_{\sigma,\pi}$ pair of states (and the accompanying destabilization of the $^{1,3}D_{\sigma,\sigma}$ partners) induced by linearization of the acyl moiety,[10] but is *thermochemically unfeasible*. As a result, neither cleavage path from the singlet can compete with intersystem crossing to the ^{3}n,π* parent. The fact that cleavage does occur from the triplet, in spite of the same thermochemical and electronic prohibitions, demonstrates the importance of the additional reaction path available to the triplet, namely, internal conversion at the crossing point A.[8b]

For cyclobutanone (Figure 2), the release of the four-membered ring strain energy[11] during cleavage results in a lowering of both pairs of $D_{\sigma,\pi}$ and $D_{\sigma,\sigma}$ states relative to the n,π* states of the parent. Therefore, *both bent and linear cleavages become thermochemically feasible*. Since there is no electronic barrier to the linear cleavage, the ^{1}n,π* state may now cleave at a rate competitive with intersystem crossing to the n,π* triplet of **1**. Cleavage of ^{1}n,π* leading to the bent diradical remains electronically forbidden.

These diagrams not only clarify points 1 and 3 above, but lead to the expectation that *major, previously unappreciated differences in nuclear motion occur when* **1** *or* **2** n,π* *undergoes homolytic cleavage*. Point 2, the contrasting behavior of the cyclobutanone and cyclohexanone n,π* triplets, may be thought of as a chemical manifestation of these differences.

The thermodynamic information we possess on the decarbonylation is the following: (a) The loss of CO from a bent acyl radical of the type R-CH₂-CO requires an activation energy of approximately 14 kcal/mol.[12] (b) The activation energy in the parent cyclobutanone reaction must be negligible since **2** undergoes decarbonylation even at 77 K (point 3). It is, however, somewhat difficult to comprehend how an equilibrated 1,4 diradical could have an activation energy less than 10 kcal/mol, the endothermicity of the decarbonylation process[13] (eq 6).

$$CH_2 \quad \dot{C}H_2 \longrightarrow CO + \dot{C}H_2 \quad \dot{C}H_2 \quad \Delta H \sim 10 \text{ kcal/mol} \quad (6)$$
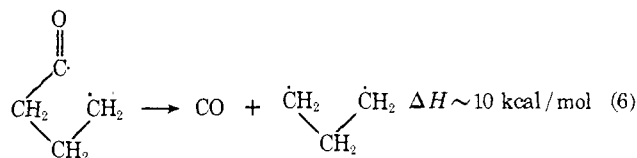
Let us pause and consider the theoretical correlation diagram for the loss of CO in the simple formyl radical case.[14] Recall that the bent $^2A'$ and linear $^2A''$ (or $^2\Sigma^-$) formyl radicals associated with a ^2S hydrogen atom respectively constitute the

familiar $D_{\sigma\sigma}$ and $D_{\sigma\pi}$ diradicals created in the α-cleavage of formaldehyde. The bent form is calculated to be ~25 kcal/mol more stable than its linear excited state.[15] However, when the C···H linkage is elongated both states correlate with an excited state of the dissociation products, $H(^2S) + CO(^3\pi)$. The ground state of these products, $H(^2S) + CO(^1\Sigma^+)$, is linked to a high-lying excited state ($^2A'$ or $2\Sigma^+$) of the formyl radical. Of the two resulting crossings one is truly allowed; the second, which involves two curves of similar A' symmetry, is avoided.[16] Figure 3 represents the behavior of this trio of states during the lengthening of the C···H distance.

As deduced earlier, the ^{3}n,π* α-cleavage of **2** can only engender the bent $D_{\sigma\sigma}$ radical. The acyl $^2A'$ bent radical must overcome an energy barrier (resulting from the avoided crossing) to reach the dissociated state $H(^2S) + CO(^1\Sigma^+)$. To achieve this an activation energy of approximately 14 kcal/mol is required. But **1** cleaves to produce the $^2A''$ linear acyl radical which is part of the $D_{\sigma\pi}$ diradical. The discrete vibrational levels of $^2A''$ have the same energy as the continuous range associated with the $^2A'$ bent ground state. The former will acquire, to a small extent, the properties of the latter.[17] Since the $^2A'$ continuum corresponds to the HCO system flying apart to give $H(^2S) + CO(^1\Sigma^+)$ the discrete vibrational levels of the linear formyl radical will, after a time, find themselves in this continuous range; that is, they will also dissociate. This situation is called a heterogeneous type I (i.e., electroic) predissociation.[18] In effect, *the α-cleavage of cyclobutanone produces a chemically activated primary product* (the linear $^2A''$ radical) *via an electronically allowed pathway*. The predissociation phenomenon is a radiationless transition responsible for decarbonylation of this primary product. This mechanism explains how the activation energy for this quasi-spontaneous rupture can be less than the parent (ground-state) bond dissociation energy.

In conclusion, Salem diagrams for α-cleavage of alkanone n,π* states reveal that two competing mechanisms should be considered. The first involves homolytic cleavage of the C–CO bond to form a diradical possessing a bent acyl fragment; the second mechanism involves homolytic cleavage of the C–CO bond to form a diradical possessing a linear acyl fragment. Only the latter is electronically allowed for a n,π* state. For unstrained ketones (**2**), however, formation of the linear acyl radical is thermochemically unrealistic. For small ring ketones (**1**) the strain energy may be employed to remove this thermodynamical handicap.[19] The linear acyl radical thus generated is expected to produce a different array of products than its bent counterpart.

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(10) The calculated stabilization of the $D_{\sigma\pi}$ singlet and triplet states is 43 kcal/mol. The parallel destabilization of the $D_{\sigma\sigma}$ states is 30 kcal/mol. The four states are degenerate (acetone case, ref 8b). The potential energy surfaces for α-cleavage of formaldehyde have also been calculated: (a) W. H. Fink, *J. Am. Chem. Soc.*, **94**, 1073 (1972); (b) D. M. Hayes and K. Morokuma, *Chem. Phys. Lett.*, **12**, 539 (1972).

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(17) This mixing of the $^2A'$ and $^2A''$ electronic states may be induced either by interaction with the rotation about the *a*-axis or by interaction with the overall rotation.

(18) Reference 14b, p 455.

(19) Other structural features which tend to stabilize the diradical but not the carbonyl excited state could similarly serve to promote α cleavage to the linear form. It may, for example, be a factor in the photochemistry of β,γ unsaturated carbonyl compounds (see, e.g., H. Schuh, E. J. Hamilton, H. Paul, and H. Fischer, *Helv. Chim. Acta*, **57**, 2011 (1974); E. Baggiolini, H. P. Hamlow, and K. Schaffner, *J. Am. Chem. Soc.*, **92**, 4906 (1970), and references therein).

(20) This laboratory is part of the Equipe de Recherches no. 549 associated with the CNRS.

Nicholas J. Turro,* William E. Farneth

Department of Chemistry, Columbia University
New York, New York 10027

Alain Devaquet*

Laboratoire de Chimie Organique Theorique²⁰
Universite Pierre & Marie Curie
75230 Paris, France
Received June 21, 1976

The Solvation of Diphenylmethyl Carbanions Using Variable Temperature Carbon-13 Magnetic Resonance

Sir:

Smid was the first to extensively investigate the thermodynamics of the equilibria between contact ion pairs and solvent separated ion pairs for fluorenyl carbanions using ultraviolet absorption spectroscopy.[1,2] UV has been extended to relatively few other carbanion systems because it requires absorptions well enough separated to be assigned to the contact ion and to the solvent separated ion.[3-7] Proton magnetic resonance has also been used to study the solvation of fluorenyl,[8,9] triphenylmethyl,[8] indenyl,[8] and diphenylallyl[10] carbanions. However, proton chemical shift changes are quite small and the most solvation-sensitive carbon may not have an attached proton. Further, proton shifts are frequently affected by other factors such as ring current and a sensitive site may be obscured by solvent resonances.
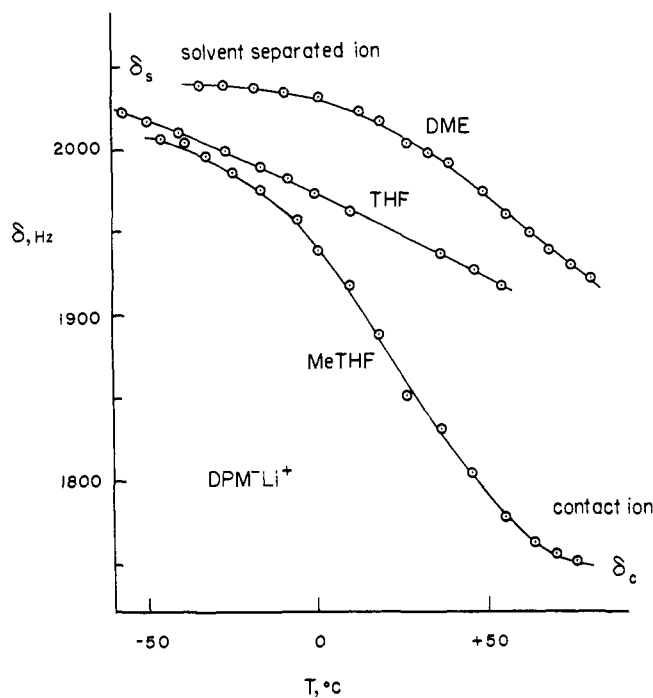

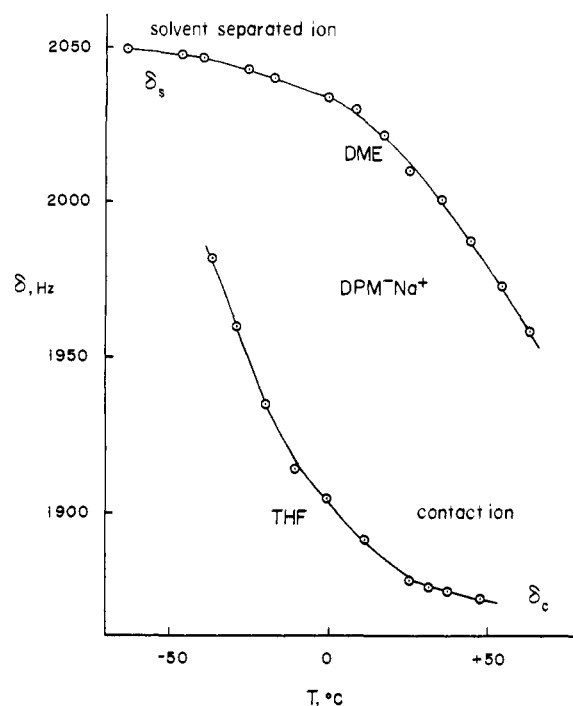**Figure 1.** The α-carbon chemical shifts for diphenylmethyllithium.

Figure 2. The α-carbon chemical shifts for diphenylmethylsodium.

We have studied the solvation process for all the alkali metal carbanions of diphenylmethane (DPM^-M^+) dissolved in 2-methyltetrahydrofuran (MeTHF), tetrahydrofuran (THF), and dimethoxyethane (DME) using variable temperature carbon-13 magnetic resonance.[11-16] Carbon-13 chemical shift changes give a sensitive overall view of the redistribution of π-electron density at each carbon as the carbanion responds to the solvation process. Very large chemical shift changes are observed for the α and para carbons with the small cations, lithium and sodium. Much smaller changes, if any, occur with potassium, rubidium, and cesium (Table I). Proton decoupled carbon-13 spectra were taken at approximately 8° increments for the carbanions that showed appreciable temperature-dependent chemical shift changes (Figures 1 and 2).[17] Unlike