Keto–Enol Tautomerism of Gas-Phase Ions. Structure of Reactive C₆H₆O Radical Cations

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Abstract: The keto–enol tautomerism of the gas–phase phenol and 1,3-cyclohexadien-5-one radical cations is postulated to explain the ion chemistry of C₆H₆O radical cations generated from ethyl phenyl ether and bicyclo[2.2.2]oct-2-ene-5,7-dione as well as direct ionization of phenol. The C₆H₆O radical cations generated from these sources were studied by measurement of metastable kinetic energy release for the reaction C₆H₆O⁺· → C₅H₆⁺· + CO. Contrary to previous reports, it is shown that both phenol and cyclohexadiene ions interconvert if they are sufficiently activated to decompose by undergoing CO loss. The phenol ions isomerize to a keto form by a high-energy sigmatropic [1,3] hydrogen shift, which is the rate-determining step for CO loss. Because of a large kinetic barrier for the ketonization, a large fraction (~20%) of excess energy in the transition state is released as kinetic energy in the decarbonylation reaction of metastable ions.

Ever since the discovery of the mass spectral rearrangement of the ethyl phenyl ether to give [C₆H₆O]⁺·,[2] this process has been the subject of a large number of investigations. In part, its importance stems from the dominant role the rearrangement assumes in the fragmentation of alkyl aromatic ethers. Furthermore, it serves as a model for rearrangement reactions in substituted aromatic compounds. In this report, new experimental evidence is given which can be interpreted to resolve many of the ambiguities associated with previous studies.

Almost all ion structural and mechanistic methods have been directed at understanding this system, including metastable abundance ratios,[3] kinetic energy release studies,[4] field ionization kinetics,[5a] isotopic labeling,[3,5] isotope effect measurements,[6] appearance potential studies,[7] ion cyclotron resonance (ICR) spectrometry,[8] and collisional activation (CA) spectrometry.[4,9] The foremost goal of these studies has been to determine the structures of "stable" and "decomposing" C₆H₆O radical cations. "Stable" ions are those which resist decomposition in the time frame of a mass spectrometer (ca. 10⁻⁵–10⁻⁶ s), whereas "decomposing" ions have been sufficiently activated to dissociate in times shorter than 10⁻⁵–10⁻⁶ s. Two structures have been proposed for [C₆H₆O]⁺·: the enol form (**1**) and the corresponding keto isomer (**2**).
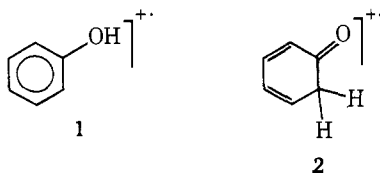
Studies of the structure of the stable ions, except for the appearance potential measurements,[7] show that direct ionization of phenol or fragmentation of ethyl phenyl ether produces a common ion, presumably **1**.[4b,8,9] Bicyclo[2.2.2]oct-2-ene-5,7-dione (**3**) expels ketene in a cycloreversion reaction
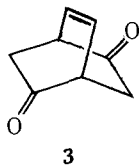
to give a different structure, presumably **2**.

If the interpretation based on the CA,[4b,9] ICR,[8] and metastable kinetic energy release[4] is accepted, then little, if any, interconversion of **1** and **2** occurs for either the stable or reactive ions.

A more fundamental question than the structure of various C₆H₆O ions is whether keto–enol tautomerism can occur for isolated gas-phase cations. As pointed out in a recent review,[10] there are no known examples of "uncatalyzed" [1,3] hydrogen shifts for radical cations within the time scale of a conventional mass spectrometer (i.e., <10⁻⁵ s). However, at longer times available with ICR spectrometry, the cyclopentanone enol ion seems to undergo ketonization.[11]

According to the Woodward–Hoffmann rules,[12] these observations are not surprising because this type of intramolecular tautomerism is a specific example of a sigmatropic [1,3] hydrogen migration, a symmetry-forbidden process. Because the application of these rules to radical cations is uncertain, we became interested in acquiring further experimental data on the energetic requirements for the [1,3] hydrogen shift.

One difficulty associated with selecting the appropriate chemical system for study is that most possess low-energy fragmentation channels which preempt a higher energy "forbidden" process. For example, the enol of the acetone radical cation has been shown to be a stable species which can be distinguished from the keto form using characteristic ion–molecule reactions[13a] and collisional activation.[13b] The quite different low-energy decompositions exhibited by ionized acetone and its enol form[13c] strongly support the lack of interconversion of these two structural isomers despite an earlier assertion that they do.[13d] We believe that the keto–enol tautomerism cannot compete with a low-energy (0.7 eV in the case of acetone[14]) dissociation channel which leads to methyl loss.

A similar situation pertains to acetophenone and its corresponding enol. Kinetic energy release measurements[15] are in accord with no tautomerism for low-energy, decomposing ions. For the acetophenone radical cation, the necessary activation for loss of a methyl radical is only 0.6 eV.[14] Methyl loss from the enol form must involve a hydrogen rearrangement, but a circuitous mechanism involving ring hydrogens occurs in lieu of the straightforward, but presumably "forbidden" [1,3] hydrogen shift.[16]

Unlike these systems, the [C₆H₆O]⁺ is well suited to investigate the possibility of tautomerism because ion **1** can accommodate high activation (~3.2 eV) before fragmenting to [C₅H₆]⁺· which is the lowest energy pathway. This energy is the difference between the appearance potential of [C₅H₆]⁺· and the ionization potential of phenol.[14] Examination of ions with approximately this excitation is possible with metastable ion methods using conventional mass spectrometry. Previous investigators have demonstrated that ion **2** releases less internal energy in the decomposition to [C₅H₆]⁺· than **1**. This has been interpreted to exclude interconversion of **1** and **2**,[4] even for ions

Table I. Kinetic Energy Release (meV) for Various C_6H_6O Ions as a Function of Lifetime of the Ion, Measured in the Reaction $[C_6H_6O]^{+\cdot} \rightarrow [C_5H_6]^{+\cdot} + CO$

| accelerating voltage, V	phenol		ethyl phenyl ether	bicyclo[2.2.2]-oct-2-ene-5,7-dione
	HV[a]	MIKES[a]		
Hitachi RMU-6D[a]				
6000	b	496	b	b
4200	494	b	515	b
4000	b	436	b	b
3600	452	b	480	355
3000	436	420	b	b
2500	414	408	430	351
2000	393	398	405	350
1500	388	b	b	b
1000	366	376	364	350
AEI MS-5076[c]				
8000	506		b	380
6000	478		b	b
4000	450		b	370
2000	410		b	b
1000	385		b	370

[a] The repeller potential at 3600 V was 10 V and was proportionately decreased with the accelerating voltage. The measurements were made for first field free region metastables using the accelerating voltage scan method (data listed as HV). The kinetic energy released was calculated from the width of the metastable peak at half-height. Precision, ±2% relative. The metastable decompositions occurring in the second field free region were made using the mass analyzed ion kinetic energy spectroscopy (MIKES); see the Experimental Section. *[b]* Not determined. *[c]* The measurements were made for second field free region metastable decompositions using a Daly detector to defocus the main beam. Each result is the average of five determinations. Precision, ±1% relative.

with high excitation, largely because **2**, a fragment ion, should release *more* energy than ionized phenol if the two species are interconverting.[17]

Results and Discussion

If the interpretation is correct that the difference in kinetic energy release implies nonequilibrating keto and enol forms for the reactive or decomposing ions, one can conclude that the $[C_6H_6O]^{+\cdot}$ system is another example of the inability of a [1,3] hydrogen shift to compete with ionic fragmentation. However, we wish to propose an alternate explanation that the larger kinetic energy released in the decomposition of **1** to give $[C_5H_6]^{+\cdot}$ is due to "nonfixed" or excess energy in that transition state. Furthermore, the excess energy arises from a rate-determining [1,3] hydrogen shift, which requires activation in excess of the energy barrier for subsequent loss of CO from **2** (eq 1). Because the ions are isolated and cannot be

$$\text{(OH)} \longrightarrow (=O) \longrightarrow C_5H_6^{+\cdot} + CO \quad (1)$$
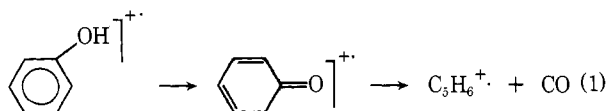
collisionally stabilized, the excess energy is carried over to the decarbonylation step and shows up as a "nonfixed" energy component in the kinetic energy release.

If this postulate is correct, C_6H_6O ions decomposing at longer times should require lower activation for the rate-determining step. This is because the rate constant for reaction of an isolated species is a function of internal energy. Therefore, the amount of "nonfixed" energy observed in the decarbonylation would decrease and may converge ultimately on the kinetic energy released for structure **2** generated directly from bicyclo[2.2.2]oct-2-ene-5,7-dione (**3**).

An alternative statement of this hypothesis is that the keto-enol tautomerism for C_6H_6O ions is subject to "kinetic shift". Kinetic shift refers to the additional activation that must be supplied to an isolated species to cause it to fragment or dissociate rapidly enough to be observed within the time constraints of the apparatus used for study. According to the quasi-equilibrium theory for unimolecular fragmentations,

kinetic shift is reasonable in this case because the transition state is "tight" and has a large energy demand.[18]

Variation of Kinetic Energy Release with Decomposition Time. An experimental test of this idea is to measure the kinetic energy release for the decarbonylation of **1** and **2** as a function of the lifetimes of the ions. The data, presented in Table I, were taken on two different double-focusing mass spectrometers, a Hitachi RMU-6D and an AEI MS-5076. Moreover, the measurements with the Hitachi were made by a normal accelerating voltage scan (HV) and by the mass-analyzed ion kinetic energy spectroscopy method (see the Experimental Section). For both instruments, the lifetime of the ion was prolonged by decreasing the accelerating voltage. An additional increase for the residence time in the source was effected by a proportional decrease in the repeller field for the experiments conducted with the Hitachi mass spectrometer. Our results at high acceleration are similar to previously published data;[4] i.e., **1** releases significantly more energy than **2**. However, as longer lived ions are sampled, the energy release appears to converge on that observed for **2** (see Figure 1). The near constancy of the energy release for **2** is expected because this ion does not have to ketonize prior to loss of CO. Furthermore, it shows that the data do not result from an experimental artifact. We believe that the results establish the rate-determining ketonization of **1** to **2** prior to decarbonylation to $[C_5H_6]^{+\cdot}$.

Each series of experiments on the different mass spectrometers produces a set of internally consistent data which demonstrates the steady decrease in energy release for **1** and the near constancy for **2**. Agreement between the two data sets is satisfactory, and the small discrepancies are probably due to instrumental conditions. For the Hitachi, the kinetic energy release was measured in the first field free region by accelerating voltage scans and in the second field free region by the MIKES method. The measurements on the MS-5076 were made for decompositions occurring after the electrostatic section (second field free region) by magnetic field scans (see the Experimental Section).

A schematic diagram of a two-dimensional slice through a potential energy surface for the C_6H_6O radical cations is shown in Figure 2. The diagram reflects our current understanding
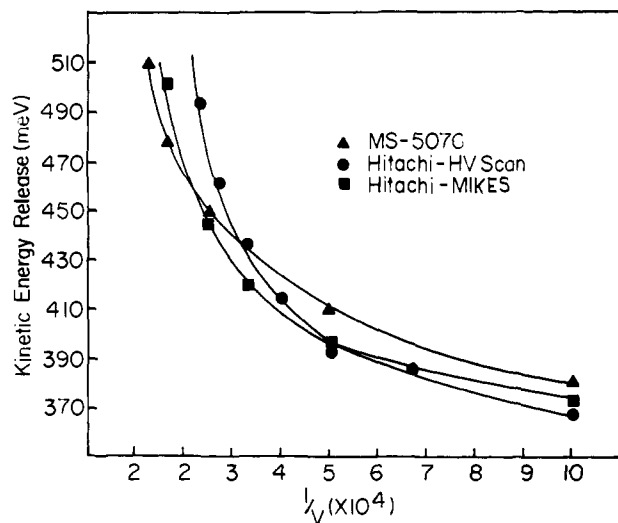
Figure 1. Variation of kinetic energy release for the reaction $[C_6H_6O]^{+\cdot}$ → $[C_5H_6]^{+\cdot}$ + CO as a function of the accelerating voltage. The source of $[C_6H_6O]^{+\cdot}$ is phenol. For comparison, structure **2** gives a nearly constant kinetic energy release of approximately 350 or 370 meV (see Table 1).

REACTION COORDINATE

Figure 2. Schematic potential energy surface for decomposition of isomeric C_6H_6O radical cations.

of the energetics for $[C_6H_6O]^{+\cdot}$. Starting on the left, the barrier height of 5.8 eV for dissociation to $C_5H_5^+$ has been determined as the difference in the ionization potential of phenol and the appearance potential of $C_5H_5^+$.[7a] Similarly, the barrier height for CO loss is established using the appearance potential for the m/e 66 ($C_5H_6^{+\cdot}$).[7a] We have remeasured this quantity and determined a value of 3.1 ± 0.1 eV using a semilogarithmic method.[7a] The difference of 1.1 eV for **1** and **2** is the difference between the experimental heat of formation of the phenol ion and the calculated heat of formation of its tautomer.[7] Finally, the barrier height for decomposition of **2** to give $[C_5H_6]^{+\cdot}$ has been measured for this report by determining the difference in the appearance potentials of $[C_6H_6O]^{+\cdot}$ and the metastable for $[C_6H_6O]^{+\cdot}$ decomposing to $[C_5H_6]^{+\cdot}$ using **3** as the precursor for $[C_6H_6O]^{+\cdot}$. A value of 1.1 eV was obtained.

If the [1,3] hydrogen shift is the slow step, the minimum internal energy required for isomerization of **1** and **2** in the source of a mass spectrometer (i.e., at times $<10^{-6}$ s) is equal to 3.1–3.2 eV. However, because of the variation of energy release, we know that excitation in excess of the barrier height (kinetic shift) is required. Therefore, the actual barrier height must be less than 3.2 eV.

To confirm this postulate, the appearance potential for the metastable ion for the loss of CO from **1** was measured and found to be 0.8 eV lower than the 3.1 eV reported above for the normal ions. Accordingly, a value of at least 0.8 eV is assigned as the kinetic shift for the decarbonylation reaction. This is reflected by the lower barrier in Figure 2 denoted as 1.3 eV above the heat of formation of structure **2**. Thus, it is clear that the barrier height of 3.2 eV for isomerization of **1** to **2** is a kinetic barrier, and the actual barrier height is considerably lower.

The dramatic variation of kinetic energy release indicates that the rate constant for loss of CO from **1** is much less dependent on internal energy than most decompositions which occur in the 10^{-5}–10^{-6}-s time frame. We can convert the observed decrease in energy release (ca. 0.12 eV) for an increase of approximately three in ion lifetime to the average internal energy variation using the relationship $\Delta\epsilon^{\ddagger} = (0.44N)\Delta T^{\ddagger}$, where $\Delta\epsilon^{\ddagger}$ is the change in internal energy required to produce a change of $\Delta T^{\ddagger}$ in kinetic energy release, and N is the number of vibrational degrees of freedom. This empirical relationship has been proposed by Haney and Franklin[19] and should be
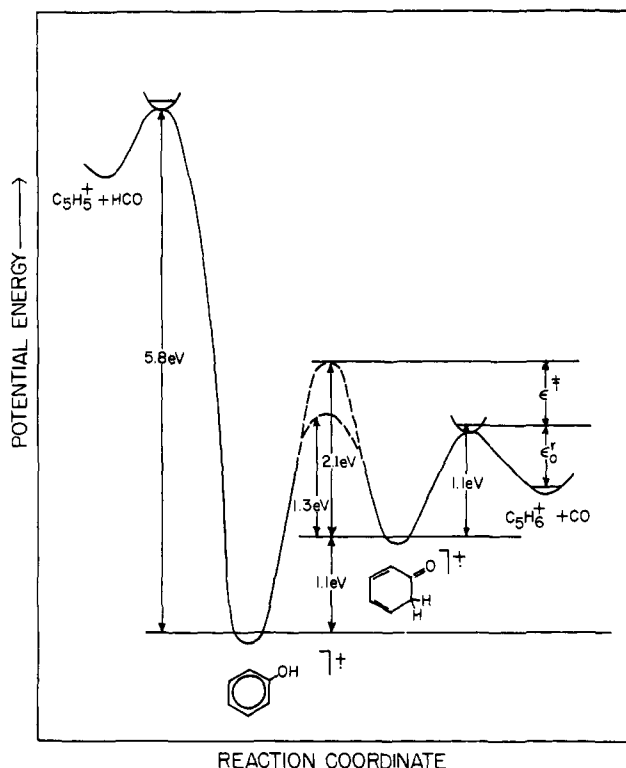
valid if statistical equilibration of the internal energy occurs prior to the dissociation. The predicted range of internal energies giving rise to a variation of 0.12 eV in energy release is approximately 1.8 eV. Because this value is significantly greater than the measured 0.8 eV which was assigned as kinetic shift, we tentatively suggest that the loss of CO occurs so rapidly after the isomerization of **1** to **2** that complete equilibration of the excess energy ($\epsilon^{\ddagger}$ in Figure 2) has not occurred.
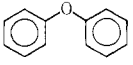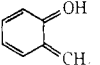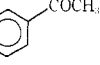
Returning to the [1,3] hydrogen shift, we note two interesting features of this process. First, the internal energy requirement is large: 2.4 eV for metastable $[C_6H_6O]^{+\cdot}$ and 3.0–3.2 eV for normal or more rapid decompositions. Second, the rate constant for the shift exhibits a surprisingly slow increase with internal excitation.

The next higher energy fragmentation channel for $[C_6H_6O]^{+\cdot}$ is loss of CHO, a process which releases approximately 150 meV of kinetic energy for both **1** and **2**. This release contains no detectable nonfixed energy by the experimental criterion used for loss of CO. Therefore, the high energy forms of **1** and **2** interconvert before decomposing to $C_5H_5^+$ without excess energy in that transition state simply because the barrier for CHO loss is higher than that for CO loss and for tautomerism.

This dramatic change in kinetic energy release over the small time range that can be sampled on a conventional mass spectrometer is, to our knowledge, an unprecedented observation. Jones et al.[20a] have compared the kinetic energy released for rapidly decomposing ions in the source of a mass spectrometer with that released by the more slowly decomposing metastable ions. In general, it is found that source fragmentations release more kinetic energy because they contain a larger component of "nonfixed" energy. However, the time span covered in this comparison is many orders of magnitude, whereas the variations reported here occur for decomposition time intervals which differ by a factor of 3 approximately.

More recently, a direct comparison has become available.[20b] A study of the kinetic energy release for metastable dissocia-

Table II. Independence of Kinetic Energy Release (meV)[a] and Decomposition Time for Selected Reactions

accelerating voltage, V	$170 \rightarrow 142$	$107 \rightarrow 79$	$148 \rightarrow 130$	$120 \rightarrow 105$
3600	425	260	215	13.6
3000				
2400	450	258	212	13.8
1500			220	
1000	448	258	218	13.1

[a] Measured by accelerating voltage scans using the Hitachi RMU-6D as discussed in Table I. Precision, ±4% relative.

tions occurring over ion lifetimes which vary by a factor of 10 shows no detectable changes. The dissociation reactions chosen for investigation, the loss of H from the benzene molecular ion and the loss of HCN from ionized benzonitrile, are processes which also are subject to significant kinetic shift.

Nevertheless, to substantiate the unique character of the variation in kinetic energy release for **1**, we have measured the translational energy liberated for four ionic decompositions which cover a wide range of energy release (Table II). Similar to the decarbonylation of **2**, these processes show no detectable variation in the kinetic energy release as a function of time. Three of the reactions were chosen because they also possess similar features to the $[C_6H_6O]^{+\cdot}$ system. The first two processes are also decarbonylation reactions which release large amounts of kinetic energy. The third reaction, loss of water from 1-tetralol, requires a rate-determining H transfer from the 4 position.[20] The final decomposition process gives little kinetic energy release (a Gaussian metastable is observed, but no detectable variation of kinetic energy release with time can be found.

Isotope Effects. A requisite of the hypothesis that a rate-determining H transfer occurs in the decarbonylation of the phenol ion is a primary isotope effect for this reaction. Howe and Williams[6] have shown that the loss of CO from *p*-bromophenol-*O-d* is accompanied by an isotope effect (k_H/k_D) of 3.1 for metastable decompositions, an observation which is consistent with O–H bond breaking in the rate-determining step. It is difficult to make similar measurements for the unsubstituted phenol ion because other fragmentations which could serve as a reference are not competitive with CO loss. Specifically, 94% of all metastable decompositions of $[C_6H_6O]^{+\cdot}$ involves CO loss. Moreover, loss of CHO from phenol-*O-d* to give *m/e* 66 ($C_5H_4D^+$) overlaps with $[D_5H_6]^{+\cdot}$ produced by CO loss from $[C_6H_5OH]^{+\cdot}$, and this prohibits measuring the isotope effect by comparing CO loss with CHO and CDO losses in a mixture of phenol and phenol-*O-d*.

Nevertheless, an assessment of the isotope effect (k_H/k_D) can be made by obtaining the ratio of ion intensities, $([C_5H_6]^{+\cdot}/[C_6H_6O]^{+\cdot})/([C_5H_5D]^{+\cdot}/[C_6H_5DO^{+\cdot}])$, in the normal mass spectrum. Because of interferences at each of these masses, the intensity data were taken using the AEI MS-5076 at a resolving power of 70 000, which is sufficient to resolve the peaks of interest. In this way, an isotope effect of 1.3 was obtained for decarbonylation reactions in a mixture of 1:3 phenol and phenol-*O-d*. Similarly, the isotope effect was measured for CO loss from $[C_6H_6O]^{+\cdot}$ and $[C_6H_5DO]^{+\cdot}$ produced from $C_6H_5OCH_2CD_3$. A value of 1.8 was obtained.

The small intensity differences are proposed to be due to primary isotope effects. They are consistent with the decomposition of a highly energized species because the magnitude of the effect is similar to that expected for a purely "classical"

isotope effect[21] (i.e., an effect determined by the differences in O–H vs. O–D bond stretching frequencies, $\nu_{OH}/\nu_{OD} = 1.37$, rather than zero-point energy differences). Accordingly, the actual barrier for a [1,3] hydrogen shift for **1** → **2** is less than 3.2 eV as was discussed previously. However, to cross the barrier within 10^{-6} s or less, additional activation is required which is manifested in the large variation of kinetic energy release reported in Table I and the "classical" hydrogen isotope effects discussed above.

Conclusion

Contrary to previous interpretations, the difference in metastable kinetic energy release for phenol (**1**) and cyclohexadienone (**2**) is *not* attributable to structural differences for reactive ions. The larger energy released by the phenol radical cation is composed of both reverse activation energy and "non-fixed" energy (ϵ_0^r and $\epsilon^{\ddagger}$, respectively; see Figure 2.). At longer times, the energy released by **1** becomes nearly equal to that of **2** which indicates that the two structures can equilibrate prior to loss of CO. We postulate that CO loss occurs from the keto form (**2**) and CHO loss results from the enol (**1**). The tautomerism is not detected for stable ions, but only for those possessing sufficient activation to undergo loss of CO. A *maximum* barrier of 2.4 eV is set for the enol–keto tautomerism of metastable phenol radical cations.[23]

Finally, the results show that structural determination of reactive gas-phase ions based on the kinetic energy release criterion[24] can be equivocal in cases where fragmentation is preceded by high-energy, rate-determining isomerization. The complicating factor which takes the form of an unpredictable quantity of nonfixed energy in the transition state, has been considered previously[25] and may be significant for ionic decompositions accompanied by large kinetic shift. Further studies are in progress to investigate the generality of this phenomenon.

Experimental Section

The metastable kinetic energy release measurements were performed on a Hitachi RMU-6D double focusing mass spectrometer modified for the accelerating voltage defocusing method[26] and on an AEI MS-5076 double focusing mass spectrometer operated in the Daly metastable mode[27] (in this mode the metastables observed decompose in the second field free region). The source was maintained at 175 °C with a nominal ionizing electron energy of 70 eV, an electron current (total emission) of 100 (Hitachi) and 500 μA (MS-5076). The MS-5076 and Hitachi are equipped with an adjustable energy resolving β slit. In the experiments where the normal accelerating voltage was changed to sample different time regions, the β slit was adjusted to maintain a constant voltage width of the normal ion beam on the Hitachi; this voltage width was 2.5 V. With the MS-5076, a β slit of 0.20 mm was employed. Wider slit widths led to apparent higher kinetic energy release values.

After the initial submission of this manuscript, the Hitachi mass spectrometer was modified to operate in the mass analyzed ion kinetic energy spectroscopy (MIKES) mode. The design was based on a previous report by Wachs et al.[28] Our modification required interchanging the source and detector, reversing the slits and polarity of the magnetic field, and outfitting the source with differential pumping (3-in. diffusion pump).

The samples of phenol and ethyl phenyl ether were obtained from standard sources. The sample purity was checked by mass spectrometry, and each was used without further purification. Phenol-*O-d* was prepared by equilibration of phenol-*O-h* with D_2O and the percent deuterium determined by low ionizing energy (11.5 eV) mass spectrometry (98% d_1, 2% d_0).

The deuterium-labeled ethyl phenyl ether was prepared by the method previously described by Nibbering.[29] The isotopic composition was determined by low ionizing energy mass spectrometry and the label position checked by ^{1}H NMR (96% d_3, 4% d_2 in the ethyl-*2,2,2-d3* phenyl ether). Bicyclo[2.2.2]oct-2-ene-5,7-dione was prepared according to the method of Takeda et al.[30a] and Grob and Weiss.[30b]

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Dimerization of the Li, Na, K, and Cs Salts of Diphenylethylene Radical Anions and the Equilibria and Kinetics of Their Formation by Attachment of Electron–Cation Pairs. The Nature of Electron–Cation Aggregates

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Abstract: Flash photolysis of Cat^+, $\overline{C}(Ph)_2CH_2CH_2\overline{C}(Ph)_2$, $Cat^+ = Cat^+,^-DD^-,Cat^+$, results in electron photoejection and yields $C(Ph)_2{:}CH_2^-{\cdot},Cat^+ = D^-{\cdot},Cat^+$, the unreduced hydrocarbon D, and the electron–cation pair e^-,Cat^+. The latter two products react and form $D^-{\cdot},Cat^+$ radical anions: $D + e^-,Cat^+ \rightleftharpoons D^-{\cdot},Cat^+$ (k_1, k_{-1}). The radical anions combine and reform the original dimer, $Cat^+,^-DD^-,Cat^+$: $2D^-{\cdot},Cat^+ \rightarrow Cat^+,^-DD^-,Cat^+$ (k_2). Kinetic studies of the reactions ensuing after a flash allow us to determine k_1, k_{-1}, k_2, and the equilibrium constant $K_1 = k_1/k_{-1}$. Their values depend on the cations' nature, namely, for Li, $k_1 = 0.9 \times 10^6$ M^{-1} s^{-1}, $k_{-1} = 15$ s^{-1}, $K_1 = 6 \times 10^4$ M^{-1}, and $k_2 = 1.2 \times 10^8$ M^{-1} s^{-1}; for Na, $k_1 = 1.9 \times 10^7$ M^{-1} s^{-1}, $k_{-1} = 33$ s^{-1}, $K_1 = 6 \times 10^5$ M^{-1}, and $k_2 = 3.5 \times 10^8$; for K, $k_1 = 4 \times 10^9$ M^{-1} s^{-1}, $k_{-1} \leqslant 20$ s^{-1}, $K_1 \geqslant 2 \times 10^8$ M^{-1}, and $k_2 = 10 \times 10^8$ M^{-1} s^{-1}; and for Cs, $k_1 \gg 10^{10}$ M^{-1} s^{-1}, $K_1 \gg 10^8$ M^{-1}, and $k_2 = 30 \times 10^8$ M^{-1} s^{-1}. The significance of these findings is discussed. The striking increase in k_1 and K_1 as the cation is varied from Li^+ to Cs^+ is noteworthy and may shed light on the nature of electron–cation aggregate.

The results of our studies of flash photolysis of the sodium salt of the dimeric dianions of 1,1-diphenylethylene in tetrahydrofuran[1] ($Na^+,\overline{C}(Ph)_2CH_2CH_2\overline{C}(Ph)_2Na^+ = Na^+,^-DD^-,Na^+$) demonstrated that the absorption of visible light results in electron photoejection

$$Na^+,^-DD^-,Na^+ \xrightarrow{h\nu} Na^+,^-DD\cdot + e^-,Na^+$$
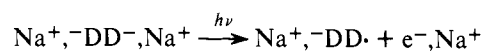
and not in photodissociation of the dimer into two radical anions:

$$C(Ph)_2{:}CH_2^-{\cdot},Na^+ = D^-{\cdot},Na^+$$

The dimeric radical anions $Na^+,^-DD\cdot$ decompose within ~1 μs into the hydrocarbon D and its radical anion $D^-{\cdot},Na^+$. Whenever the excess of D is large, electron capture is rapid and virtually quantitative

$$D + e^-,Na^+ \rightleftharpoons D^-{\cdot},Na^+ \qquad (1)$$

and the simple dimerization

$$2D^-{\cdot},Na^+ \rightarrow Na^+,^-DD^-,Na^+ \qquad (2)$$

is observed in the dark period, i.e., the reciprocal of $\Delta(OD)$ monitored at any wavelength is linear with time.