∠O2′-C spiro-O4′, 109 (1)°; ∠O2′-C spiro-C6, 104 (1)°; ∠C2-C spiro-C6, 117 (1)°; ∠C2-C spiro-O4′, 109 (1)°.

A single example of this type of oxidative photoaddition has been observed in the photooxidation of a plastoquinone model system.[7] The most appealing of several plausible mechanisms for the formation of these trioxanes is outlined in Scheme II. The attack of an n,π^* state of *p*-benzoquinone upon COT should lead to the triplet diradical species **9** ↔ **10**, which would presumably have a significant lifetime before spin inversion made possible collapse to the 1,4-adduct **1**. If this triplet species has a sufficiently long lifetime,[8] it might be trapped by molecular oxygen to form the 1,2,4-trioxane **7**. Since molecular oxygen exists as a ground state triplet, it is conceivable that this trapping might proceed in a concerted fashion and might be viewed as a form of triplet–triplet annihilation. Both **7** and **1** are stable under the irradiation conditions in acetic acid, and yet neither of these products is observed in this solvent. The absence of **7** might be indicative of a reduced lifetime of **9** ↔ **10** in acidic media, and the absence of **1** might indicate that protonation also alters the mode of collapse of **9** ↔ **10** in such a way as to form **5** and **6** directly. Perhaps this occurs through the ion **11**.

Finally, it should be noted that these reactions are not the results of some exotic property of the laser radiation. However, products such as **7** cannot be prepared in more than trace amounts with the more usual near-ultraviolet light sources, since they are destroyed nearly as fast as they are formed. Filtered sources may be used, but then the light intensity can be so drastically attenuated that the accumulation of appreciable amounts of product can require long irradiation times. Under these conditions **1** and **7** can undergo significant decomposition which greatly hampers their isolation. Thus, a laser light source, while not essential to an investigation of this nature, simplifies the task considerably.

A full account of this and related work will be forthcoming.

Acknowledgments. We express our appreciation to the Petroleum Research Fund, administered by the American Chemical Society, for financial support of this work, to Mr. Robert J. Weber, Jr., for his able laboratory assistance, and to Badische Anilin und Sodafabriken for their most generous gift of COT.

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(8) J. A. Barltrop and B. Hesp, *J. Chem. Soc.*, 5182 (1965).

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−*E* Mass Spectra

Sir:

We describe a new type of mass spectrum which is the result of converting positively charged to negatively charged ions in the analyzer of the mass spectrometer. Preliminary results suggest that these mass spectra may be valuable in characterizing the structures of both positively and negatively charged ions.

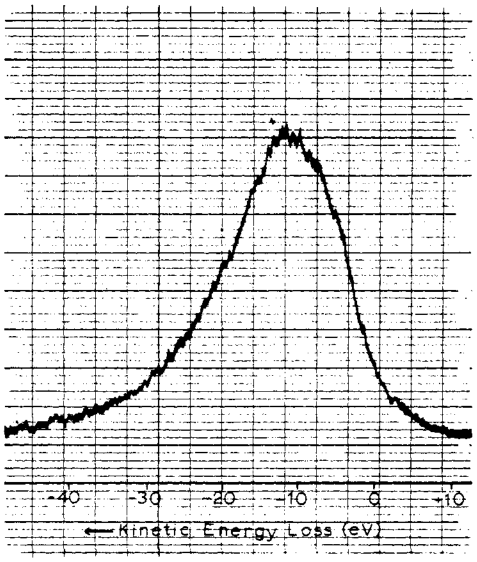

Figure 1. Kinetic energy spectrum of the beam of negatively charged ions generated from positively charged benzene ions (energy 8 keV) by collision with benzene vapor.

In earlier work we have employed high-energy (keV) ion–molecule reactions occurring in the analyzer of the mass spectrometer to effect charge stripping[1] (1) and

$$m^+ + N \longrightarrow m^{2+} + N + e \qquad (1)$$

charge exchange[2] (2). These two reactions can be used

$$m^{2+} + N \longrightarrow m^+ + N^+ \qquad (2)$$

(N is any neutral gas or vapor)

to provide a wealth of information on the internal energies of ions, on thermochemical quantities such as double ionization potentials, and on ion–molecule reaction mechanisms at high energy.[3] Moreover, reactions 1 and 2 each form the basis for a new type of mass spectrum, $E/2$ and $2E$ mass spectra,[4] respectively. The analytical potential of doubly charged ion mass spectra ($2E$ spectra) has already been explored in some detail[2] and $E/2$ spectra are under study in this regard.

Consider a double-focusing mass spectrometer of Nier–Johnson geometry[5] operated at ion accelerating voltage V and electric sector voltage E and equipped with a detector at the point of energy focus, *i.e.*, between the electric and magnetic sectors. If the polarities of the electric sector plates are reversed (the $-E$ condition) but all other voltages left unchanged, then only negatively charged ions of kinetic energy eV will be transmitted by the electric sector and detected. Moreover, all such negatively charged ions must have been generated from positively charged ions in the field-free region preceding the electric sector. Figure 1 shows the kinetic energy distribution of the negatively charged ions

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(1) (a) R. G. Cooks, J. H. Beynon, and T. Ast, *J. Amer. Chem. Soc.*, **94**, 1004 (1972); (b) T. Ast, J. H. Beynon, and R. G. Cooks, *ibid.*, **94**, 6611 (1972).

(2) (a) J. H. Beynon, R. M. Caprioli, W. E. Baitinger, and J. W. Amy, *Org. Mass Spectrom.*, **3**, 455 (1970); (b) J. H. Beynon, A. Mathias, and A. E. Williams, *ibid.*, **5**, 303 (1971); (c) T. Ast, J. H. Beynon, and R. G. Cooks, *ibid.*, **6**, 741, 749 (1972).

(3) J. H. Beynon, R. M. Caprioli, R. G. Cooks, and G. R. Lester, "Metastable Ions," Elsevier, Amsterdam, in press.

(4) So called because the electric sector in a double-focusing mass spectrometer is operated respectively at one-half and twice the potential (E) normally used to obtain mass spectra.

(5) Our experiments were done using the Hitachi RMH-2 mass spectrometer, modified as previously described.[1b]

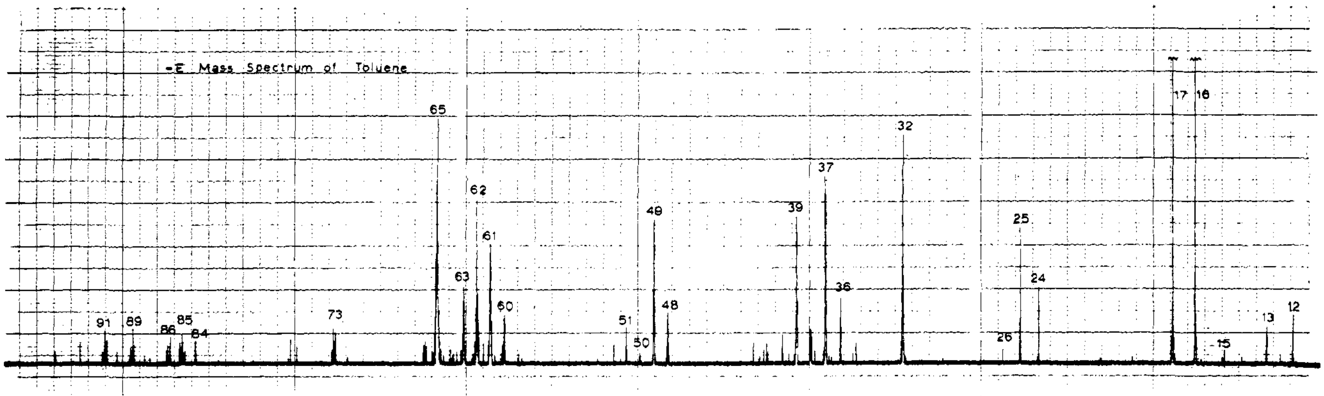

Figure 2. $-E$ mass spectrum of toluene taken using toluene as collision gas. A single scan is shown to illustrate the signal to noise characteristics of the spectrum. The major ions are discussed in the text. Note that the ions of mass 16, 17, and 32 are associated with air and not with toluene. The total ion current is about 10^{-4} that of the corresponding positive ions.

generated when benzene (2.5×10^{-5} Torr) is used as sample and as collision gas (1.3×10^{-4} Torr). The negative ion current is approximately 10^{-5} of the positively charged ion current and the most probable kinetic energy is some 10 eV lower than that of the positive ions.[6] Hence the reaction is accompanied by conversion of kinetic energy to internal energy.

If the β detector is now raised so as to transmit the beam of negative ions and the polarity of the magnet reversed, then the beam can be mass analyzed and the $-E$ mass spectrum obtained.[7] Figure 2 shows such a spectrum for toluene. The spectrum resembles neither the normal positive ion spectrum nor the negative ion spectrum[8] of toluene, although it has some major ions in common with both. The most abundant ions are *m/e* 65 (the aromatic cyclopentadienyl anion?), *m/e* 61, 49, 37, and 25 (the anions of sp carbon acids), *m/e* 48, 36, and 24 ($C_n\cdot^-$, $n = 2, 3, 4$) and *m/e* 39 ($C_3H_3^-$). The ions $C_n\cdot^-$ and C_nH^- have previously been observed to be abundant in the spectra of negative ions generated in the ion source.[7]

We have obtained $-E$ spectra on a variety of compounds using the substance itself as collision gas. The following are some highlights of these results. (1) Benzene gives abundant $C_n\cdot^-$ and C_nH^- ions. The abundance of C_6H^- (25% relative abundance, ~8% total ion current) is remarkable since the corresponding positive ion has a relative abundance of 0.1% (~0.05% of the total ion current). The cross section for this charge permutation reaction must be relatively high; by contrast, $C_6H_6\cdot^+$ gives no detectable amount of $C_6H_6\cdot^-$. The influence of negative ion stability on these results is apparent. (2) The most abundant ions in the anisole $-E$ mass spectrum are *m/e* 65 ($C_5H_5^-$) and *m/e* 93 ($C_6H_5O^-$). Neither of these ions is abundant in the negative ion mass spectrum reported by Djerassi and coworkers.[8] (3) Although C_3H^- occurs (65% relative abundance) in the spectrum of *n*-heptane, hydrogen-rich ions $C_3H_3^-$ (100%) and $C_3H_5^-$ (33%) are much more in evidence than in the spectra of aromatic compounds. (4) A major ion in the spectra of both acetone and ethyl acetate occurs at *m/e* 41, probably, C_2HO^-.

Although the mechanism of the charge permutation reaction is not known, some observations can be reported. The basic reaction has been studied briefly by Melton[9] and by White and coworkers.[10] Durup and colleagues[11] have studied electronic energy levels in neutral species by using them as targets for the conversion of H^+ to H^-. They observed two distinct processes, one linear in collision gas pressure, the other quadratic.

In each case we have investigated, a first-order dependence upon collision gas pressure was observed. Most of these experiments were done without mass analysis (*e.g.*, carbon tetrachloride using air as collision gas), but a linear relationship between collision gas pressure (benzene) and negative ion abundance was also observed for *m/e* 93 in anisole.

These results suggest that the mechanism may be eq 3 which would mean that the kinetic energy loss and

$$m^+ + N \longrightarrow m^- + N^{2+} \qquad (3)$$

the cross section for the reaction should depend upon the double ionization potential of the collision gas. In agreement with this conclusion it was found that while $C_6H_5O^+$ generated from anisole readily gave $C_6H_5O^-$ using 1×10^{-4} Torr of benzene as target species, the same pressure of helium did not give a detectable signal. A detailed interpretation of the kinetic energy loss spectra accompanying charge permutation reactions will be given elsewhere. It also seems likely that electron affinities can be determined from the kinetic energy losses associated with reaction 3, and this is currently being explored.

We believe that the most valuable results of $-E$ mass spectra and associated kinetic energy measurements may lie in the new information that they provide on the structures of positively charged ions in the mass spectrometer. An abundant ion in the $-E$ spectrum is

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(6) The zero energy loss position for the negative ion beam is taken as the same as that for the positive ion beam. This is justified by the fact that the electric sector voltages were identical (to 1 mV in 300 V) and by the fact that translation of the source slit across the ion beam produced no detectable effect upon the distribution shown in Figure 1.

(7) Although the energy resolving β-slit must be narrow for kinetic energy measurements such as that shown in Figure 1, it is advantageous to use a wide slit (0.3 mm in our experiments) to plot $-E$ mass spectra at adequate sensitivity.

(8) R. T. Alpin, H. Budzikiewicz, and C. Djerassi, *J. Amer. Chem. Soc.*, 87, 3180 (1965).

(9) C. E. Melton, "Principles of Mass Spectrometry and Negative Ions," Marcel Dekker, New York, N. Y., 1970, pp 234, 269.

(10) F. M. Rourke, J. C. Sheffield, W. D. Davis, and F. A. White, *J. Chem. Phys.*, **31**, 193 (1959).

(11) J. Appell, P. G. Fournier, F. C. Fehsenfeld, and J. Durup, presented at 20th Annual Conference on Mass Spectrometry and Allied Topics, American Society for Mass Spectrometry, Dallas, Texas, 1972.

associated with a particularly stable negative ion structure. But the conversion from positive to negative ion is very rapid;[12] hence, the corresponding positive ion must have essentially the same structure. Hence, only if the positively charged ion possesses a certain structure will an abundant negatively charged ion be observed. For example, the occurrence of $C_5H_5^-$ in high abundance in the anisole spectrum suggests that $C_5H_5^+$ is cyclic rather than linear, although more experiments, particularly with homologous ions, will be necessary to establish this conclusion firmly. The reverse procedure, inference of negative ion structures from well-established positive ion structures, should also be possible.

Acknowledgment. We wish to thank the National Science Foundation for generous support under Grant No. GP 32187 and Dr. J. H. Bowie for helpful discussions.

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(12) For a one-step mechanism the relative velocity of the species is such that, for an ion of mass 100, 5 Å is covered in 10^{-13} sec.

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Photochemical Rearrangements of Pyrylium Cations[1]

Sir:

Photolysis of 2,6-disubstituted-4*H*-pyran-4-ones results in photoreactions typical of α,β-unsaturated carbonyl compounds. Thus, both 2,6-diphenyl- and 2,6-dimethyl-4*H*-pyran-4-one (I) undergo photodimerization, presumably *via* their n,π^* excited states, to yield their respective head-to-tail cage dimers.[2,3] Pyrone I has also been shown to undergo photoaddition reactions with alkynes to yield 1:1 cyclobutene adducts.[4] Recently, however, Ishibe and colleagues have reported that 2,6-disubstituted-3,5-diphenyl-4*H*-pyran-4-ones undergo photoisomerizations more characteristic of cross-conjugated cyclohexadienones to yield 3,6-diphenyl-4,5-disubstituted-2*H*-pyran-2-ones.[5] Lack of photodimerization in these latter cases was attributed to steric effects of the 3,5 substituents rather than to any change in the nature of the excited states involved in the reactions.

As part of our program to investigate the effects of protonation on the course of the photoreactions of carbonyl compounds, we wish to report that photolysis of 2,6-dimethyl-4-hydroxypyrylium ion (II), formed by protonation of I in 96% H_2SO_4, results in the formation of a mixture of 4,5-dimethyl-2-hydroxypyrylium ion (III) and 5,6-dimethyl-2-hydroxypyrylium ion (IV). Neutralization of the resulting solution converted ions III and IV to 4,5-dimethyl-2*H*-pyran-2-one (V) and 5,6-dimethyl-2*H*-pyran-2-one (VI), respectively. Subsequent experimental evidence showed that III was an intermediate in the photoisomerization of II to IV.

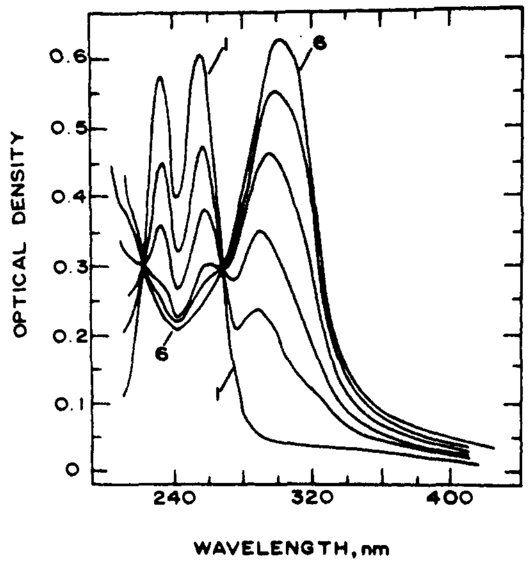
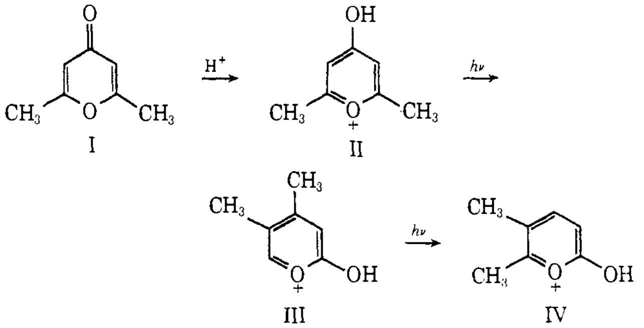


Figure 1. Ultraviolet absorption spectrum of II, 5×10^{-5} *M* in 96% H_2SO_4: 1, before irradiation; 2-6, after consecutive 15 min irradiations at 253.7 nm.



Solution of I in 96% H_2SO_4 resulted in the formation of thermally stable II from which I could be quantitatively recovered by neutralization.[6] Figure 1 shows the successive changes in the absorption spectrum of II following short duration irradiations with light of 254 nm at ambient temperature.[7] The figure illustrates the gradual disappearance of II with the simultaneous increase in absorbance at longer wavelengths ultimately reaching a maximum at 304 nm. The final product (λ_{max} 304 nm) seems to be both thermally and photochemically stable under these conditions. The absorption spectrum of a solution of II irradiated to any per cent conversion remained unchanged after standing in the dark for extended times. This testifies that the changes in Figure 1 are photochemical with no interference from thermal reactions. Considering the three species present in the reaction solution, *i.e.*, II, III, and IV, the isosbestic points at 221 and 267 nm in Figure 1 indicate only a coincidental equality of their extinction coefficients at those wavelengths.

Preparative-scale photolysis[8] of II, 3.2×10^{-3} *M* in 96% H_2SO_4, followed by neutralization led to the isolation of V and VI, which were separated by preparative gas chromatography. Re-solution of V and VI in 96% H_2SO_4 regenerated III and IV, λ_{max} 287 and 304

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(1) Presented in part at the Sixth Great Lakes Regional Meeting of the American Chemical Society, June 1972, Houghton, Mich., Abstract 43.

(2) P. Yates and M. J. Jorgenson, *J. Amer. Chem. Soc.*, **80**, 6150 (1958).

(3) N. Sugiyama, Y. Sato, and C. Kashirma, *Bull. Chem. Soc. Jap.*, **43**, 3205 (1970).

(4) J. W. Hanifin and E. Cohen, *J. Org. Chem.*, **36**, 910 (1971).

(5) N. Ishibe, M. Odani, and M. Sunami, *Chem. Commun.*, 1034 (1971).

(6) Cation II: λ_{max} 254 nm (ϵ 12,200), 232 nm (ϵ 11,600).

(7) Bausch and Lomb high intensity monochromater with 125-W high-pressure Hg arc.

(8) Preparative-scale photolyses were carried out under nitrogen in a 230-ml Pyrex vessel fitted around a quartz low-pressure Hg lamp with output of 2.5 W.