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RELATIVE STABILITIES OF MONO- AND DIOXOLENIUM IONS

John W. Larsen, Sheila Ewing, and Marilyn Wynn[1]
Department of Chemistry,
University of Tennessee
Knoxville, Tennessee, 37916

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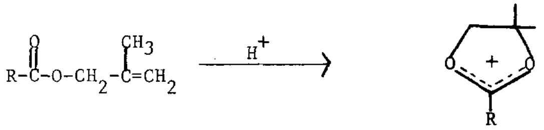
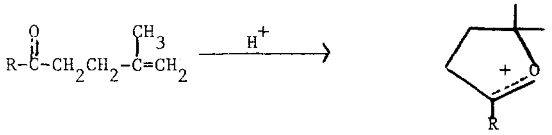
We report herein the first measurements of the relative stabilities of a series of 1,3-dioxolenium ions and oxolenium ions. The heats of formation of the aforementioned ions from unsaturated esters and ketones have been measured calorimetrically in 99.5% sulfuric acid and in fluorosulfonic acid. In this system several groups which are thought to stabilize carbonium ions by resonance interact as strongly with the precursors as with the oxolenium ions. This gives rise to the observation that the heat of formation of oxolenium ions from ketones is more exothermic than the heat of formation of dioxolenium ions from esters.

The 1,3-dioxolenium ions (I) and oxolenium ions (II) are formed by the processes shown below.



(I)



(II)

These processes have been well documented and the ions are formed quite cleanly.[2,3,4] The structures of these ions have been amply verified using nmr by several other groups of workers[4,5] and in our own laboratories. In all cases we could detect no side products.

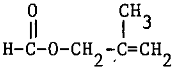
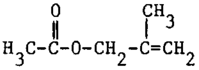
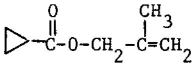
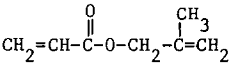
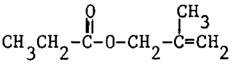
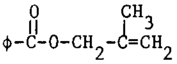
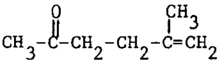
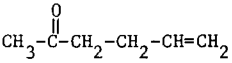
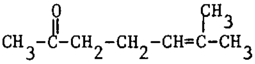
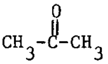
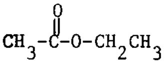
The relative heats of formation[6] of these ions from the indicated precursors together with several other ions included for comparison purposes are reported in Table 1. The 2-methyl-1,3-dioxolenium ion formed from compound 2 and the 2-cyclopropyl-1,3-dioxolenium ion (3) have essentially the same relative heats of formation from the esters. It is well known that the cyclopropyl group has a great stabilizing effect on carbonium ions. In this system it apparently stabilizes the ester precursor to the same extent as the dioxolenium ion. In the cases of the phenyl (compound 6) and vinyl (compound 4) substituted dioxolenium ions, the ion is destabilized with respect to the starting material when compared with the methyl substituted ion. In the case of the phenyl group, the bulk of the substituent could be causing some of this destabilizing due to the effects of increasing ionic size on the interactions of the ion with the solvent[7]. However, this explanation will not hold for the vinyl substituted ion as demonstrated by a comparison with the heat of formation for the ethyl substituted ion (compound 5). In this case the vinyl group apparently stabilizes the starting ester by resonance much more than it stabilizes the resulting dioxolenium ion. It also has been observed that the interaction of phenyl groups with carbonyl groups appears to be greater in aldehydes and ketones than in the protonated aldehydes and ketones.[8]

Oxolenium ions have been generated from ketones 7, 8, and 9. It is apparent that the relative heats of formation of the mono-oxolenium ions from the ketone are 4 kcals/mole more exothermic than the heats of formation of the dioxolenium ions from the esters. One expects the dioxolenium ion (I) to be more stable than the oxolenium ion (II). Thus replacing the methylene group in the ketone by an oxygen atom (giving the ester) confers a greater stability on the precursor than it does on the resulting ion.

The oxolenium and dioxolenium ions are quite stable species. Their heats of formation from the appropriate precursors are at least 10 kcals per mole more exothermic than the heats of protonation of esters and ketones. Their formation is approximately 15 kcals per mole more exothermic than the heat of protonation of diphenylethylene.

Hart[8] has shown that the chemical shifts of the ring protons in 1,3-dioxolenium ions correlate well with σ values for substituents on a phenyl group in the two position on the

Table 1. Heats of Formation of 1,3-Dioxolenium Ions and Oxolenium Ions From the Esters and Ketones in 99.5% H_2SO_4 at 25°

	Compound	$\Delta\bar{H}_{SCCl_4}$ Kcal/mole	$\Delta H_{obs,H_2SO_4}$ Kcal/mole	$\Delta H_{obs,FSO_3H}$ Kcal/mole
1.	 $H-\overset{O}{\overset{\|}{C}}-O-CH_2-\overset{CH_3}{\overset{\mid}{C}}=CH_2$	+0.99 ± .06	-20.1 ± 0.6	
2.	 $H_3C-\overset{O}{\overset{\|}{C}}-O-CH_2-\overset{CH_3}{\overset{\mid}{C}}=CH_2$	+0.72 ± .03	-23.7 ± 0.2	-31.5 ± 0.4
3.		+0.10 ± .01	-23.6 ± 0.3	
4.	 $CH_2=CH-\overset{O}{\overset{\|}{C}}-O-CH_2-\overset{CH_3}{\overset{\mid}{C}}=CH_2$	+0.45 ± .02	-19.2 ± 0.7	
5.	 $CH_3CH_2-\overset{O}{\overset{\|}{C}}-O-CH_2-\overset{CH_3}{\overset{\mid}{C}}=CH_2$	+0.67 ± .03	-23.0 ± 0.2	
6.	 $\phi-\overset{O}{\overset{\|}{C}}-O-CH_2-\overset{CH_3}{\overset{\mid}{C}}=CH_2$	+0.62 ± .11	-22.1 ± 0.3	-28.6 ± 0.2
7.	 $CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-\overset{CH_3}{\overset{\mid}{C}}=CH_2$	+0.46 ± .05	-27.7 ± 0.2	
8.	 $CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-CH=CH_2$	+0.26 ± .03	-26.3 ± 0.1	
9.	 $CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-CH=\overset{CH_3}{\overset{\mid}{C}}-CH_3$	+0.06 ± .07	-27.0 ± 0.4	
10.	 $CH_3-\overset{O}{\overset{\|}{C}}-CH_3$	+0.79 ± .02	-12.3 ± 0.1	-19.1 ± 0.1
11.	 $CH_3-\overset{O}{\overset{\|}{C}}-O-CH_2CH_3$	+0.05 ± .02	-12.0 ± 0.1	
12.	$\phi_2C=CH_2$	+0.1 ± .07		-14.7 ± 0.2[a]

a) E. M. Arnett and J. V. Carter, unpublished data.

dioxolenium ring. A plot of our relative heats of formation versus his reported chemical shifts for the ions reported in Table 1 and several other dioxolenium ions generates a scatter diagram. This is not surprising since we are measuring an energy difference between a ground state and an ion while Hart is measuring a property of the ion only. We are continuing our investigation of this and similar systems including the formation of dioxolenium ions in carbohydrates and the study of cyclic cations containing other hetero atoms.

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