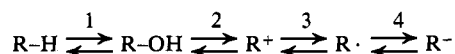


Electrochemical Determinations of pK_a 's. Triphenylmethanes and Cycloheptatriene

Sir:

Recently we reported¹ a new method for determining pK_a 's of hydrocarbons, and applied this to a determination of the pK_a of triphenylcyclopropene. The essential point was that the thermodynamics of direct conversion of a hydrocarbon to its conjugate base could also be determined from the thermodynamics of indirect conversion, through the sequence



Step 1 is the only step for which data are not easily obtained. We assume that the difference in heat of formation of a hydrocarbon and its related alcohol is constant, at least for closely similar compounds. For step 2, the commonly available thermodynamic parameter is the pK_{R^+} . For steps 3 and 4, the $E_{1/2}$'s for successive addition of two electrons can be determined by a variety of electrochemical techniques, of which cyclic voltammetry is particularly convenient in obtaining reversible potentials with very reactive species.

Recently Volz and Lotsch² have reported $E_{1/2}$'s for the one-electron reduction of a series of substituted triphenylmethyl cations. For eight of their cations, pK_{R^+} 's had also been determined by Deno,³ and these are listed in Table I. In order to apply our method we also require $E_{1/2}$ for the second reduction, of radical to carbanion, but in the series listed in Table I this is likely to be almost constant. The substituents listed will interact most strongly with the carbonium ion, not the radical, so the substituent effect on the potential for two-electron reduction of cation to anion should be found almost entirely in the first wave. We have confirmed this by the finding that under the conditions previously described¹ the potential for reduction of radical to anion is constant at -0.41 V *vs.* sce, within 0.03 V, for triphenylmethyl, 4-methoxytriphenylmethyl, and 4,4'-dimethoxytriphenylmethyl.

Given the constancy, in this series, of energy changes for steps 1 and 3, we can calculate the pK_a 's shown in Table I. The method uses a standard compound, unsubstituted triphenylmethyl, to fix the scale; thus all pK_{R^+} 's are referred to the pK_{R^+} of -6.63 for triphenylmethyl cation,³ while pK_a 's are relative to a value of 33⁴ for triphenylmethane. A typical calculation is that for the tris-*p*-methoxyphenyl system: the cation is 7.45 pK units more stable than trityl; the first electron adds at 0.47 V more negative potential than in trityl; the second electron is assumed to go in at the same potential as in trityl (as we have shown in two related cases); therefore the substituents increase the cation-anion energy gap by $0.47 \times 23 = 10.81$ kcal/mol or 7.83 pK units; thus the anion is 0.4 pK unit less stable than trityl, so its pK_a is 33.4.

All the pK_a 's are calculated to be almost the same, starting from cations whose pK_{R^+} 's range over 17 units. This is strong support for the validity of this new method of determining pK_a 's, since these substituents should not

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Table I. Triphenylmethyl Cations and Anions

4,4',4'' substituents	pK_{R^+} ^a	$E_{1/2}$ (first electron) ^b	Calcd pK_a
None	-6.63	+0.27	33.00
Trichloro	-7.74	+0.38	32.3
Monomethoxy	-3.40	+0.07	33.1
Trimethoxy	+0.82	-0.20	33.4
Tris(dimethylamino)	+9.36	-0.79	34.7
Trimethyl	-3.56	+0.05	33.6
Triisopropyl	(-6.51)	+0.07	(36.2)
Tri- <i>t</i> -butyl	(-6.5)	+0.13	(35.2)

^a Reference 3. ^b Reference 2.

perturb the energy of the carbanion much. The variations in pK_a 's may reflect real substituent effects in the carbanions (*e.g.*, in the trichloro derivative), or they may result from errors in our assumptions or in the experimental pK_{R^+} 's or reduction potentials.

We have also applied our technique to tropylium. By cyclic voltammetry, using the system described previously,¹ we find the first $E_{1/2}$ at -0.17 V *vs.* sce (lit.² -0.17 V by dc polarography) and the second wave with $E_{1/2} -0.91$ V. Combining this with the two potentials for triphenylmethyl, and the pK_{R^+} 's for the two systems, indicates that the pK_a for tropylium anion is 36, three units above triphenylmethyl anion. Dauben had also estimated⁵ $pK_a = 36$ from equilibration experiments.

These results confirm the validity of our method of determining pK_a 's, and point to wide-ranging applications of the technique. They also support our previous observation, by this method, that the lower limit pK_a for triphenylcyclopropenyl anion is 51. This remarkably high pK_a was of course inaccessible by any other technique.⁶

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The Total Synthesis of Loganin

Sir:

The naturally occurring iridoid glucoside loganin is a key intermediate on the biosynthetic pathway to the *Corynanthe*, *Aspidosperma*, *Iboga*,¹⁻³ and *Ipecacuanha*⁴ alkaloids. Its structure and stereochemistry was recently established as 1⁵⁻⁸ and confirmed by X-ray analysis.⁹

We now wish to describe a total synthesis whose key step allowed the construction of the methyl tetrahydro-

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