

# GROUND STATES OF CONJUGATED MOLECULES—XIV<sup>1</sup> REDOX POTENTIALS OF QUINONES\*

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**Abstract**—The semiempirical SCF MO procedure of Part XII<sup>1</sup> of this series has been used to calculate relative redox potentials for a series of 25 quinones for which experimental data are available. There is an excellent correlation between the calculated and observed values.

THE redox potentials of quinone–hydroquinone couples present a theoretical problem, which has aroused considerable interest, attempts having been made to interpret them in terms of HMO theory by relating them to static properties of the quinone or hydroquinone (bond order,<sup>3</sup> free valence<sup>4</sup>) or to the difference in resonance energy<sup>5</sup> between them. These attempts have, however, suffered from the known inadequacies of the HMO method and there is clearly a need for the matter to be reinvestigated in terms of some more rigorous approach.

Recent work in these laboratories<sup>2,6</sup> has led to the development of a semiempirical SCF MO method which enables the heats of formation of conjugated molecules to be calculated with remarkable precision, the differences from experiment rarely exceeding the claimed limits of experimental error. We have now applied this procedure to the problem of quinone redox potentials.

The redox potential (*RP*) of a given oxidation-reduction system is given by:

$$\Delta G = -nF(RP) \quad (1)$$

where  $\Delta G$  is the difference in free energy between the two states of the system,  $n$  the number of electrons gained or lost, and  $F$  is the Faraday constant. If it can be assumed that the differences in entropy between corresponding quinones and hydroquinones are constant, Eq. (1) can be written in the form:

$$RP = a\Delta H + b \quad (2)$$

where  $\Delta H$  is the difference in heat of atomization between the quinone and hydroquinone,  $b$  is a constant, and

$$a = -1/nF$$

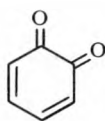
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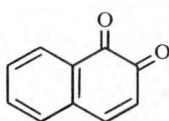
The neglect of entropy effects in connections such as this is of course a familiar procedure;<sup>7</sup> here it is further justified by the fact that the entropies of reduction of quinones are all very similar,<sup>8</sup> and by the success of an analogous procedure in the case of a related problem, i.e. the interpretation of the basic strengths of conjugated carbonyl compounds.<sup>1</sup> The difference in heats of atomization ( $\Delta H$ ) between a given quinone and the corresponding hydroquinone can of course be calculated by our SCF MO procedure.<sup>2-6</sup>

Table 1 shows heats of atomization calculated for 25 different quinones and hydroquinones for which redox potentials have been reported, together with the values of  $\Delta H$ . The observed potentials are listed in the last column of the table.

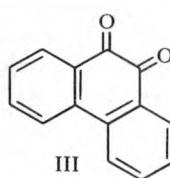
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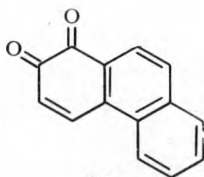
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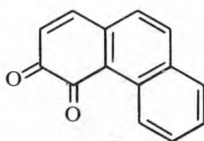
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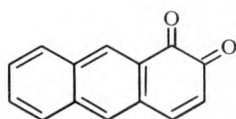
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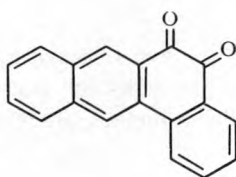
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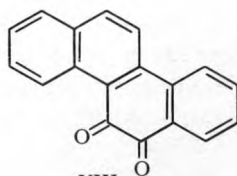
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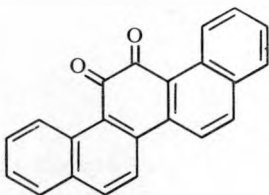
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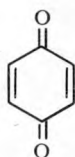
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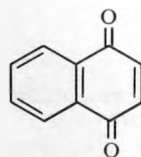
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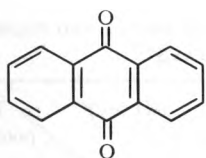
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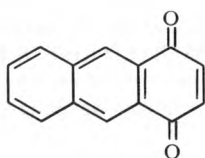
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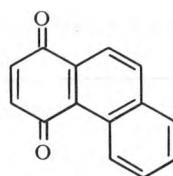
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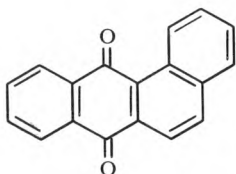
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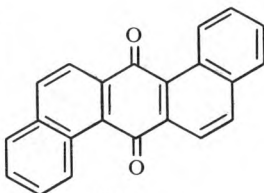
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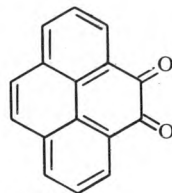
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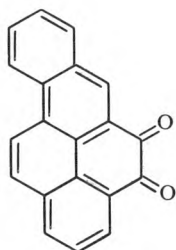
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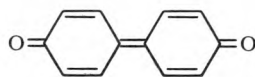
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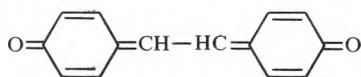
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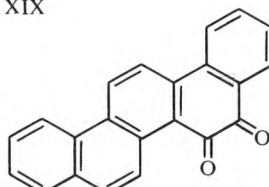
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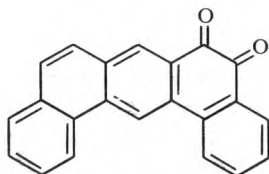
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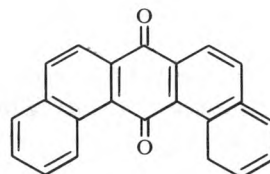
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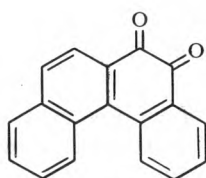
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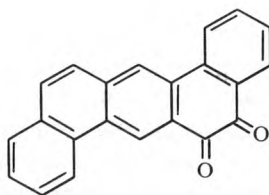
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TABLE I. CALCULATED HEATS OF ATOMIZATION OF QUINONES, SEMIQUINONES AND HYDROQUINONES AND OBSERVED REDOX POTENTIALS

Molecule	Calculated heat of atomization (eV)			$\Delta H$ (eV) <sup>a</sup>	Redox potential (V) <sup>b</sup>
	Quinone form	Semiquinone form	Hydroquinone form		
I	60.0048	62.6040	66.1278	-6.1230	0.792
II	93.8977	96.8699	99.5718	-5.6741	0.576
III	27.7918	130.6970	133.1760	-5.3842	0.460
IV	127.3503	130.5934	133.1903	-5.8400	0.660
V	127.3678	130.6368	133.1917	-5.8239	0.621
VI	127.3770	130.6687	132.8549	-5.4779	0.490
VII	161.2695	164.3545	166.5313	-5.2618	0.430
VIII	161.2547	164.4379	166.7390	-5.4843	0.465
IX	194.7219	198.0855	200.3243	-5.6024	0.503
X	60.0937	62.4128	66.1572	-6.0635	0.715
XI	94.0894	96.9371	99.6041	-5.5147	0.484
XII	128.0552	130.8513	132.8868	-4.8316	0.154
XIII	127.6034	130.7535	132.8890	-5.2856	0.401
XIV	127.5219	130.6955	133.2222	-5.7003	0.523
XV	161.4926	164.4827	166.5746	-5.0820	0.228
XVI	194.9289	198.1066	200.2320	-5.3031	0.442
XVII	142.2174	145.4300	147.5761	-5.3587	0.474
XVIII	175.7704	179.1523	181.0550	-5.2846	0.442
XIX	112.0565	116.0099	118.7635	-6.7070	0.954
XX	130.8369	135.0967	137.5088	-6.6719	0.854
XXI	194.8683	198.0550	200.3001	-5.4318	0.451
XXII	194.8736	197.9520	200.1870	-5.3134	0.455
XXIII	194.9282	198.0703	200.2320	-5.3038	0.452
XXIV	161.2377	164.2894	166.7367	-5.4990	0.492
XXV	194.8766	198.0019	200.1869	-5.3103	0.446

<sup>a</sup>  $\Delta H$  is the difference in heat of atomization between the quinone and hydroquinone form.

<sup>b</sup> Experimental oxidation-reduction potentials of quinones are taken from E. J. Moriconi, B. Rakoczy, and W. F. O'Connor, *J. Org. Chem.* **27**, 2772 (1962). See there other refs.

Fig. 1 shows a plot of  $RP$  vs.  $\Delta H$ . The points all lie close to a straight line, the correlation coefficient being 0.97 and the standard deviation in  $RP$  only 0.0197V. The correlation is much better than any of those previously reported and the present treatment has the further advantage of being based on a much more reliable theoretical approach.

The reduction of a quinone to a hydroquinone requires two electrons; hence  $n = 2$  in Eq. (1). If  $\Delta H$  is expressed in eV, as here, a plot of  $RP$  vs.  $\Delta H$  should then be a straight line of slope  $1/n$ , or one-half. The slope of the line in Fig. 1 is in fact somewhat less than this (0.39).

Similar discrepancies have been observed in analogous treatments of protonation in conjugated carbonyl compounds<sup>1</sup> and aromatic hydrocarbons,<sup>6b</sup> in each case a plot of  $pK_a$  vs. the calculated difference in energy between the base and conjugate acid was linear, but the slope was only one-half that predicted. These discrepancies were

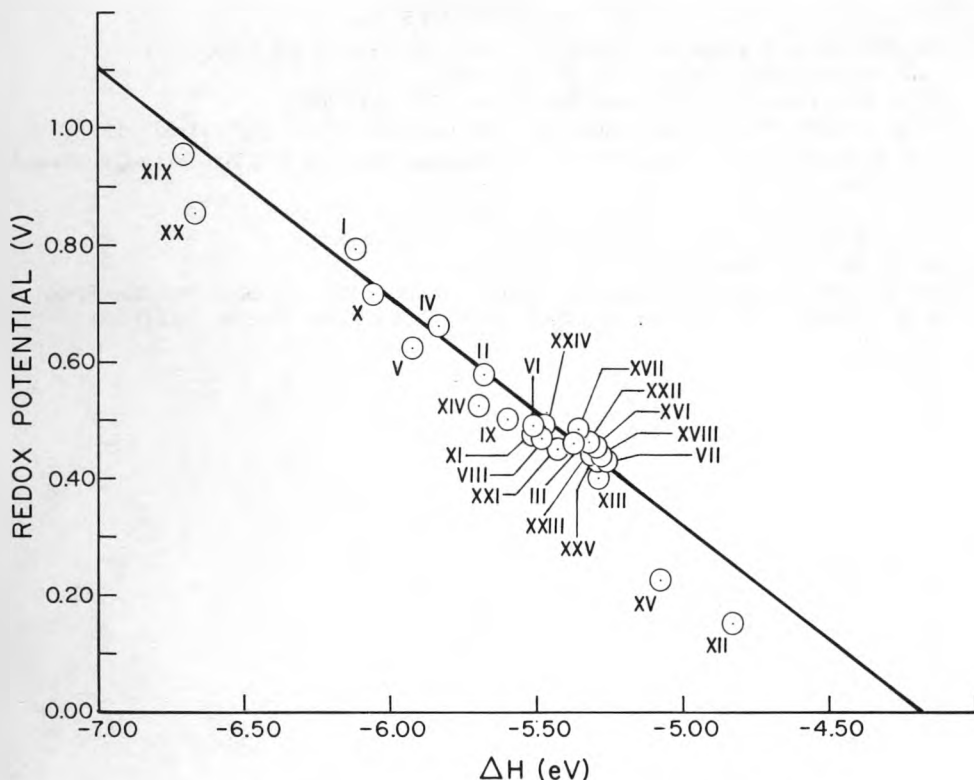


FIG. 1. Plot of redox potential vs.  $\Delta H$  for the quinones I-XXV.

attributed to differential effects of solvation. The solvation energies of neutral molecules are relatively small, so differences between different carbonyl compounds, or between different hydrocarbons, should not be important; the solvation energies of ions on the other hand are large, so differences in solvation energy here could have a much larger effect. It was shown<sup>1,6b</sup> that such differences might be expected to attract the overall energies of protonation in the right direction to explain the observed discrepancy. Similar effects could apply to the equilibrium between quinones and hydroquinones, though here they should be much smaller since both species are neutral; this could account for the slope of the line in Fig. 1 differing from the theoretical value, and for the fact that the deviation ( $\sim 20\%$ ) is so much less than in the case of the protonation reactions.

The calculations above refer of course to redox potentials measured under acidic conditions where the hydroquinone exists as such and where the intermediate semiquinone radical is reduced immediately; under alternative conditions,  $\Delta H$  and  $n$  in Eqs. (2) and (3) should refer the semiquinone ion,  $n$  being one. For completeness, we also calculated the heats of atomization of semiquinones by the half-electron method.<sup>9</sup> The results are also shown in Table 1. It should be noted that the corresponding difference in heats of atomization between the quinones and semiquinones ( $\Delta H^\ddagger$ ) do not correlate with the reported redox potentials.

## REFERENCES

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<sup>b</sup> C. de Llano, Ph.D. Dissertation, The University of Texas (1968).
- <sup>7</sup> see e.g. M. J. S. Dewar, *Advan. Chem. Phys.* **8**, 65 (1965).
- <sup>8</sup> see e.g. B. Pullman and A. Pullman, *Quantum Biochemistry*, p. 475. Interscience, New York (1963).
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