[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

REDUCTION POTENTIALS OF QUINONES
III. THE FREE ENERGY OF REDUCTION REFERRED TO THE GASEOUS STATE

BY JAMES B. CONANT

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The reduction potentials of a series of chloro- and alkyl benzoquinones were given in the first paper of this series.[1] The reduction potential of each quinone was measured in dilute aqueous solution, dilute alcoholic solution and in a solution saturated with respect to both the quinone and hydroquinone.[2] The question was raised at that time as to what should be considered the standard state for purposes of comparing the effect of different substituents on the free energy of reduction (reduction potential) of the quinone. It was pointed out[3] that the most significant results would be those obtained by the use of a solvent in which both the quinone and hydroquinone molecules were free from solvation or association; "in other words, in a solvent in which the conditions of a perfect gas are realized." Obviously, if one can calculate the free energy change referred to the gaseous state, the result will be a very close approximation to the ideal.[4] To enable such calculations to be made, Dr. A. S. Coolidge very kindly undertook to measure the vapor pressures of 6 quinones and the corresponding hydroquinones by means of his very sensitive pressure gage. His results are published in full elsewhere;[5] only the final results will be referred to in this paper.

In Table I are given Dr. Coolidge's results for the vapor pressures of benzoquinone and hydroquinone and four chloro derivatives as well as xyloquinone and xylohydroquinone. The results are all for 25° and were obtained for the most part by extrapolation from several values obtained at somewhat higher temperatures. These vapor-pressure measurements together with the values given in the first paper[6] for the reduction potential, referred to the solid state (π_s), give the free energy change of the following process (Equation 1).

$$\underset{\text{gas, 1 atm.}}{\text{quinone}} + \underset{\text{gas, 1 atm.}}{H_2} \longrightarrow \underset{\text{gas, 1 atm.}}{\text{hydroquinone}}$$

$$\underset{\text{(gaseous state, 25°)}}{-\Delta F_g} = 2F\pi_s - RT \ln P_Q/P_H \qquad (1)$$

[1] Conant and Feiser, THIS JOURNAL, **45**, 2194 (1923).

[2] In those cases in which a solid quinhydrone separated, the reduction potential of a solution saturated with quinone and hydroquinone was calculated from the measurement of saturated quino-quinhydrone and hydro-quinhydrone cells.

[3] Ref. 1, pp. 2195, 2211.

[4] If the deviations of the quinone vapor and the hydroquinone vapor from the state of a perfect gas are the same, no approximation is involved.

[5] Coolidge and Coolidge, THIS JOURNAL, **49**, 100 (1927).

[6] Ref. 1, p. 2208, Table I.

(P_Q and P_H are the vapor pressures of the quinone and the hydroquinone, respectively, at 25°.)

TABLE I

CALCULATION OF THE REDUCTION POTENTIAL REFERRED TO THE GASEOUS STATE 1 atm., 25°

Quinone	V. p. of quinone, 25°, microns	V. p. of hydroquinone, 25°, microns	0.0295 log P_Q/P_H, volts	π_s from previous paper, volts	π_g 25°, 1 atm., volts
Benzoquinone	98	0.018	0.111	0.681	0.570
Chloroquinone	40	.21	.067	.678	.611
2,6-Dichloroquinone	3.5	.027	.062	.698	.636
Trichloroquinone	0.32	.063	.021	.670	.649
Tetrachloroquinone	.0051	.0030[a]	.007[a]	.664	.657[a]
p-Xyloquinone	10	.0045	.096	.582	.486

[a] If, in the extrapolation of the vapor-pressure curve of tetrachlorohydroquinone to 25°, the same temperature coefficient as that of the other hydroquinone is employed, these values would be slightly changed with the result that π_g would be 0.650. Dr. Coolidge estimates the probable error in the vapor-pressure measurements to be such that the probable error in π_g is ±0.003 volt.

For convenient comparison with the previous results, the results may be expressed as potentials instead of free energies; the reduction potential referred to the gaseous state π_g is given by Equation 2.

$$\pi_g = \pi_s - 0.0295 \log P_Q/P_H \qquad (2)$$

The values for π_g (1 atm., 25°) are given in the last column of Table I.

In Fig. 1 the potentials are plotted against the number of substituents; the results referred to alcoholic solution (A), aqueous solution (B) and the solid state (C) are from the first paper. It will be noted at once that the effect of substituting hydrogen by chlorine is to *raise progressively and regularly the potential referred to the gaseous state* (D). This is in marked contrast to the irregularities of π_s and the peculiar rise and fall of the curve denoting the potential measured in solution. On the other hand, the effect of two alkyl groups is practically the same no matter which of the four standard states is chosen for reference.

The peculiar effect of the introduction of chlorine atoms in first causing a rise of potential (referred to the solution) and then a fall, leads one to suspect that two factors are at work. Indeed, it was the hope that this might be the case which led to the determination of the vapor pressures. The results are most gratifying.

There seems no escape from the conclusion that the free-energy change referred to the gaseous state is a measure of the affinity of the quinone molecule for the hydrogen molecule. The effect of introducing alkyl groups is to diminish this affinity, the effect of introducing chlorine atoms is to increase regularly this affinity though each subsequent substitution has less effect than the previous one. When the solid state is taken as a basis of comparison, one is measuring not only the effect of a substituent on the

affinity of the quinone molecules for hydrogen, but also the effect on the affinity of the quinone and hydroquinone molecules for each other. In the case of the alkyl quinones these last two effects practically cancel but this is not the case with the chloro derivatives. A study of Dr. Coolidge's results (Table I) shows that the irregularities of the potential referred to the solid state are probably to be attributed chiefly to the peculiar effect of continued chlorine substitution on the affinity of the hydroquinone molecules for each other. The vapor pressures of the chloroquinones decrease regularly with increasing number of chlorine atoms but the relationship in the hydroquinones is most irregular.

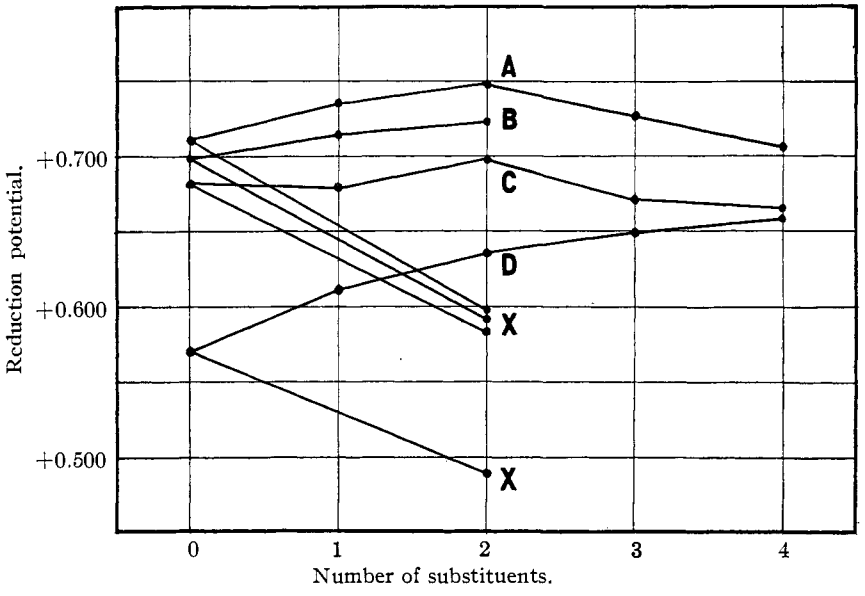

Fig. 1.—The effect of substituents on the reduction potential of derivatives of benzoquinone. The reduction potentials of the chloro derivatives referred to 95% alcoholic solution, aqueous solution, solid state and gaseous state are given by the lines A, B, C and, D respectively. The points marked by X are for xyloquinone.

There is nothing surprising, perhaps, in the fact that regularities manifest themselves in the free-energy relationships referred to the gaseous state which are absent when the solid state is taken as a standard. The more interesting observation concerns the choice of a dilute solution as a reference state. This leads to different relations from those manifested in the gaseous state (compare A and D, Fig. 1), and furthermore, the relationship is simplest in the nearly ideal state. This seems to show quite clearly that though we are dealing with very dilute (0.001 *M*) solutions of non-electrolytes, the alcoholic solutions of either chloroquinone or chlorohydroquinone (or perhaps both) are far from ideal. Both solutions con-

tained hydrochloric acid (1.0 *N*), and possibly this concentration of acid is partially responsible for the abnormality, since we have found that the pontential changes somewhat with change in acid concentration. The progressive introduction of chlorine atoms into the benzoquinone and hydroquinone nuclei in some way changes the affinity of the molecules for the solvent and this change is different for the quinone on the one hand and the hydroquinone on the other. In the case of xyloquinone and xylohydroquinone either the solutions are more nearly ideal or the introduction of two alkyl groups affects both the quinone and hydroquinone similarly.

The result of this investigation would seem to have implications which extend beyond the subject of the reduction potentials of quinones. Whenever it is possible to measure the equilibrium of an organic reaction, one is confronted with the same problem which was raised in the course of this work. From the standpoint of the organic chemist, one is interested in relating structure and free-energy changes (equilibrium constants or potentials). What one usually measures is the effect of substitution (or change of structure) not only on the free-energy change of the chemical reaction but on the affinity of the molecules of the reactants and products for each other or for the solvent. For practical purposes this sum total effect is the important thing. However, in attempting to unravel the complexities of organic chemistry it is probably desirable to separate the several factors. When such separation has been accomplished and the corresponding generalizations between structure and free-energy changes have been developed, each particular case should be readily handled. This investigation shows that referring the free energy change to some convenient standard state such as a pure liquid or pure solid, may obscure important relationships between structure and free-energy changes. Judging from the results with the chloroquinones, the most hopeful line of attack is to obtain data in regard to the free-energy changes of organic reactions referred to the gaseous state. If this is not possible a dilute solution is probably to be preferred to the pure solid or liquid.

TABLE II

FREE AND TOTAL ENERGY CHANGES REFERRED TO THE GASEOUS STATE

1 atm., 25°

Quinone	ΔF_g from Table I, cal.	ΔH_s from previous paper, cal.	Diff. in heats of sublimation of hydroquinone and quinone, cal.	ΔH_g, cal.	$T\Delta S$ gaseous state, cal.
Benzoquinone.....	−26,300	−41,300	+9800	−31,500	−5,200
Chloroquinone.....	−28,200	−41,400	+8100	−33,300	−5,100
2,6-Dichloroquinone...	−29,350	−42,700	+5300	−37,400	−8,050
Trichloroquinone.....	−29,950	−41,900	+3000	−38,900	−8,950
Tetrachloroquinone....	−30,300	−41,100	−2400	−43,500	−13,200
p-Xyloquinone.....	−22,400	−34,900	+5700	−29,200	−6,800

In addition to the free-energy change, we may calculate the total energy change referred to the gaseous state by utilizing Dr. Coolidge's values for the heats of sublimation of each quinone and hydroquinone. The results are given in Table II and for comparison $\Delta F_g(2F\pi_g)$ as well as the latent heat of the reaction ($T\Delta S$), $\Delta F_g - \Delta H_g = -T\Delta S$. The values for ΔH_s are those recorded in the first paper of this series;[1] they were calculated from the temperature coefficient of the reduction potential referred to the solid state. As was pointed out at that time, these values are not in accord with the direct calorimetric measurements except in the case of benzoquinone. A consideration of the probable errors in the thermochemical and electrochemical methods makes it extremely probable that our values are more nearly correct than those obtained by determining the heats of combustion of the quinones and hydroquinones.[7]

It will be noted that the introduction of chlorine appears to increase both ΔH_g and $T\Delta S$, while the introduction of two alkyl groups has little effect on the latent heat of the reduction and the value of ΔH_g. Considering the probable error of the determination of the sublimation heats (about 5%) and the temperature coefficient of the solid cells, the values for ΔH_g may be in error by as much as 10%. Because of these uncertainties, not much significance can be attached to the variations in $T\Delta S$ in Table II.

Summary

1. The free energy of reduction referred to the gaseous state of benzoquinone, four chloro derivatives and xyloquinone may be calculated from Dr. Coolidge's measurement of the vapor pressures of these substances and the hydroquinones and from the reduction potential referred to the solid state.

2. Such calculations (expressed as a reduction potential referred to the gaseous state) show that the effect of substituting hydrogen by chlorine is to raise progressively the potential. The substitution of two alkyl groups lowers the potential. The relation between structure and reduction potentials of the chloro derivatives referred to the gaseous state is simpler than if a dilute solution is taken as the standard state.

3. It is suggested that similar considerations may apply with many other organic compounds. The effect of substitution on the energy change of a reaction if possible should be referred to the gaseous state, as otherwise simple relations may be obscured.

4. The total energy change and the latent heat of the reaction referred to the gaseous state have been calculated.

CAMBRIDGE 38, MASSACHUSETTS

[7] Schreiner [*Z. physik. Chem.*, **117**, 57 (1925)] has made an exhaustive thermodynamic study of the quinone-hydroquinone system. His results are in good agreement with our earlier measurements. Thus, for π_s^{25} his value is 0.6805 (our value 0.681). For ΔH_s he finds 42,470 from the heats of combustion, and 42,034 from the electrical measurements; our value was 41,300.