TABLE V

INFLUENCE OF TEMPERATURE ON THE QUENCHING CONSTANTS IN GLYCEROL–WATER MEDIA

Eosin = 5×10^{-5} M; KI = 0.10 M; μ = 0.10.

Temp., °C.	Dielectric constant	η, poise	k_Q, (exp.)	k_Q (theor.) (Calcd. by eq. 12)	$1/p = k_{Q(\text{theoretical})}/k_{Q(\text{exp})}$
25	78.5 (water)	0.00895	3.24[a]	36.31	11.21
	75	.0119	2.25[a]	29.10	11.55
	65	.0414	1.06	10.48	9.90
	55	.2121	0.37	2.88	7.79
35	65	.0190	1.44[a]	22.28	15.46
	55	.0814	0.68[a]	7.16	10.42
45	65	.0106	2.69	38.90	14.47
	55	.0368	1.01[a]	14.63	14.48

[a] Check runs were made in these cases only. Reproducibility was between 1 and 2%.

An equation for the calculation of the difference between chemical energy of activation and the diffusional energy of activation has been developed by Williamson and La Mer,[4] namely

$$\log\left(\frac{1}{p} - 1\right) = \log\frac{C}{P} + \frac{(E_a - E_d)}{2.3R_gT} \qquad (14)$$

where p is the probability of reaction per encounter, C and P are orientation or entropy factors for diffusion and reaction, respectively, R_g is the gas constant and E_a and E_d are the chemical and diffusional energies of activation, respectively. A plot of $\log\left(\frac{1}{p} - 1\right)$ against $1/T$ will have a positive slope if $E_a > E_d$, a negative slope if $E_a < E_d$ and a zero slope of $E_a = E_d$. The intercept will be a measure of the relative magnitude of the steric factors of diffusion and reaction. Using the values of $1/p$ listed in Table V, plots of $\log((1/p) - 1)$ *versus* $1/T$ are shown in Fig. 5 for the isodielectric mixtures with dielectric constant values of 65 and 55. In the case of the D 55 mixtures, the slope is negative over the whole temperature range, indicating that

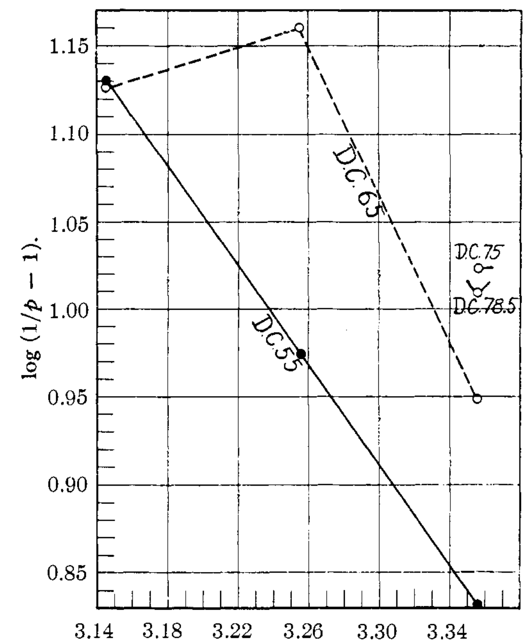

Fig. 5.—The probability of quenching per encounter as a function of the temperature.

the existing energy of activation is less than the existing energy of diffusion. The value of $(E_a - E_d) = -6500$ cal., and the intercept $\log(C/P) = 5.59$, from which $C/P = 3.9 \times 10^5$. Since C is approximately unity,[4] P becomes 2.56×10^{-6}.

In the case of the D 65 mixtures, the slope changes sign over the temperature range investigated. This change in sign can be interpreted to mean that in those mixtures there is a change in the relative importance of the two energy of activation terms over the temperature range investigated.

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[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 1567]

The Structure of Vaporized p-Benzoquinone

BY STANLEY M. SWINGLE[1]

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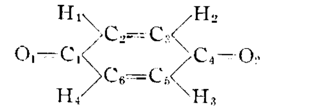
An electron diffraction investigation of the structure of vaporized p-benzoquinone has led to results consistent with those for related compounds, but differing from the values reported for the crystalline material. On the assumption of symmetry D_{2h} and C–H = 1.08 Å., the results are C=C = 1.32 ± 0.04 Å., C–C = 1.49 ± 0.04 Å., C=O = 1.23 ± 0.04 Å., and $\angle C_2C_1C_6$ = 116 ± 3°.

A length of 1.47 Å. for the conjugated C–C bond in glyoxal and dimethylglyoxal has been reported by LuValle and Schomaker,[2] indicating that resonance gives these bonds about 20% double bond character. The C=O bond length (1.20 Å.) was about the same as that in the unconjugated formaldehyde[3a] and acetaldehyde.[3b] It would be expected that the results of a similar resonance in p-benzoquinone would be apparent in its C–C bond and that the C—C=O bond angle would be nearly the same as in glyoxal and dimethylglyoxal (123°). However, Robertson[4] reported for crystalline p-benzoquinone the symmetrical, planar structure I with $C_1{=}O_1$ =



(I)

(1) Deceased October 5, 1953.

(2) J. E. LuValle and V. Schomaker, THIS JOURNAL, **61**, 3520 (1939).

(3) (a) D. P. Stevenson, J. E. LuValle and V. Schomaker, *ibid.*, **61**, 2508 (1939); (b) D. P. Stevenson, H. D. Burnham and V. Schomaker, *ibid.*, **61**, 2922 (1939).

(4) J. M. Robertson, *Proc. Roy. Soc.* (*London*), **A869**, 106 (1935).

1.14 Å., C_1–C_2 = 1.50 Å., C_2=C_3 = 1.32 Å. and $\angle C_6C_1C_2$ = 109°, a configuration which, in comparison with the substances just mentioned, would seem anomalous in regard to the C=O distance and the angle. This paper reports an electron diffraction investigation of vaporized *p*-benzoquinone. The structure found is consistent with our knowledge of related molecules.

Experimental.—Eastman Kodak Co. white label *p*-benzoquinone was photographed using a high temperature nozzle[5] in the diffraction apparatus described by Brockway.[6] Pictures were taken at camera distances of 10.75 cm. and 20.15 cm. using electrons of wave length 0.0614 Å., as determined by calibration with gold foil (a_0 = 4.078 Å.), without special correction for variable film expansion. Features extending to q values of 85 were observed ($q = 40/\lambda \sin \theta/2$).

Interpretation.—Curve V (Fig. 1) is a composite representation of the appearance of the photographs as agreed upon by two observers on the basis of examinations on several occasions extending over a period of years. Unmeasured features beyond the ninth maximum, shown as a broken line, were observed on superimposed dense photographs, but were used only for qualitative comparison with the theoretical scattering curves. Using visually estimated intensities, $I(q)$, of the maxima and minima, a radial distribution function was evaluated for the equation

$$rD(r) = \sum_i I(q_i) \exp(-aq_i^2) \sin\left(\frac{\pi}{10} q_i r\right)$$

where $\exp(-aq^2) = {}^1/_{10}$ for the last term (q_i = 58), corresponding to the last measured feature (maximum 9) of the diffraction pattern. The radial distribution curve, R of Fig. 1, shows isolated maxima at 4.10 and 3.57 Å., corresponding to C_1–O_2 and C_2–O_2, respectively, as well as several composite maxima. These two distances give $\angle C_6C_1C_2$ from 114 to 118° if it is assumed that C_1–C_2 is between 1.54 Å., the accepted single bond length, and 1.39 Å., the value for 50% double bonds. The heavy vertical lines in Fig. 1, representing the various distances in the finally accepted model, agree well with the radial distribution curve.

Theoretical intensity curves based on the equation[7]

$$I(q) = \sum_{i\ j} \frac{Z_i Z_j}{r_{ij}} \sin\left(\frac{\pi}{10} q r_{ij}\right)$$

were drawn for various symmetrical, planar (D_{2h}) models with C–H = 1.08 Å. (temperature factors ignored), C=C = 1.34 Å. and $\angle H_1C_2C_1 = \angle C_6C_1C_2$. The parameter C–C was varied from 1.44 to 1.54 in steps of 0.02 or 0.04 depending on the extent of qualitative agreement of the resulting curves with the observed scattering, while C=O was varied from 1.18 to 1.28 by the same increments and $\angle C_6C_1C_2$ was varied from 112 to 120° in steps of 1 to 3°. Best agreement was obtained for curve A (Fig. 1) which deviates noticeably from the visual curve only in the following details. The small peak seen on curve A just inside the feature designated as maximum 1 is missing from curve V. Actually this ring had been noticed by one observer, but was omitted from the visual curve because of uncertainty. Similarly the characteristic breadth of the eighth maximum, apparent on curve A but not indicated on V, had been observed on one occasion. The exaggerated prominence of the third and seventh maxima, both of which appear as shoulders on prominent features, is probably an error of interpretation, errors of this type being rather common, and accordingly does not seem to represent serious disagreement with A. Placing the thirteenth maximum too high on the slope of the fourteenth is also not surprising for a feature as dimly visible as this. The quantitative comparison for model A is shown in Table I.

TABLE I

Min.	Max.	$q_{obs.}$	q_A	$q_A/q_{obs.}$[a]
	1	10.6		
2		13.8	13.6	(0.982)
	2	17.7	18.3	(1.034)
3		21.7	22.0	(1.013)
	3	24.2	23.9	(0.986)
4		26.6	25.6	(0.963)
	4	29.6	29.0	(0.980)
5		32.3	31.4	0.973
	5	35.1	34.6	.986*
6		38.5	38.1	.990
	6	41.1	41.5	1.009
7		43.3	43.0	(0.994)
	7	45.6	44.7	(0.980)
8		48.1	47.0	0.977*
	8	51.5	50.7	.985*
9		54.5	54.1	.993
	9	58.2	57.3	.985
			Av.	.988
			Av. dev.	.009

[a] Values in parentheses were omitted in calculating the average, and starred values were given double weight.

In order to assign significant limits of error to the determination, curves for neighboring models showing imperfect agreement with the observed scattering were studied, some of which are shown (Fig. 1) as examples of the extent to which the observers feel that disagreement might result from their faulty interpretation of the visual appearance.

The most extensive range of acceptable distances for a given angle, is for models with an angle of 116°; six of the curves, including the best curve, are shown in the figure. The features of the curves are most sensitive to variations of the parameters in which the ratio C=O/C–C is changed. Thus curve B is definitely unacceptable, especially in regard to the sixth and seventh maxima, where C, with both of these bond lengths increased by relatively large amounts, is on the border of acceptability although maximum 9 seems less prominent than actually observed. In curve D, for which C–C is only 0.02 Å. greater than in C, maxima 7 and 9 have become depressed to an unacceptable extent. In the opposite direction from the best model, curve E is just beyond the range of acceptability, particularly in regard to the relative strengths of the eighth and ninth maxima. Curve F is considered barely within the limits of uncertainty. The shape parameters for these models, expressed as C=O/

(5) L. O. Brockway and K. J. Palmer, THIS JOURNAL, **59**, 2181 (1937).

(6) L. O. Brockway, *Rev. Mod. Phys.*, **8**, 231 (1936).

(7) P. A. Shaffer, Jr., V. Schomaker and L. Pauling, *J. Chem. Phys.*, **14**, 659 (1946).

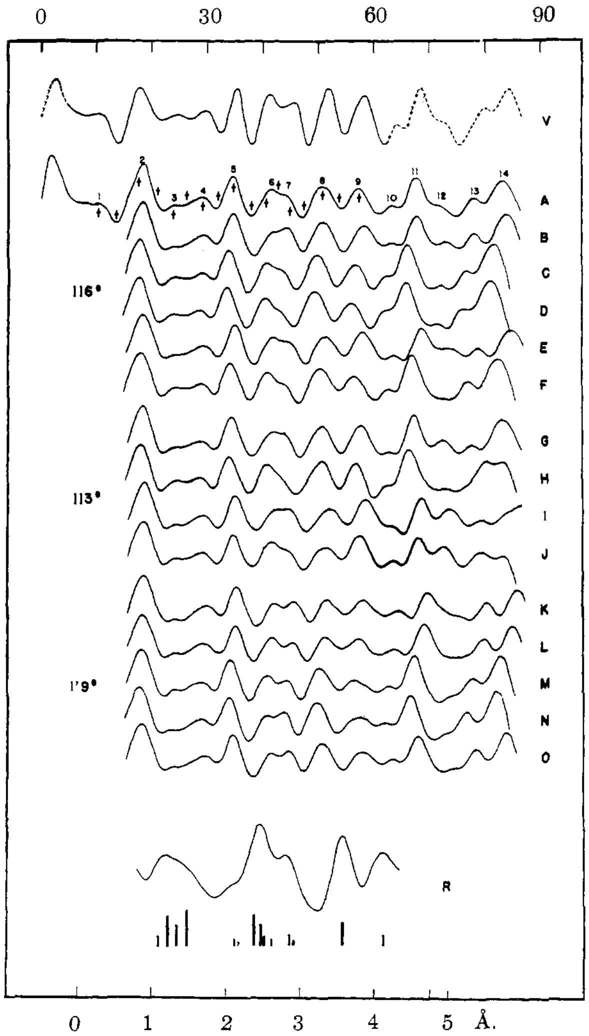


Fig. 1.—Electron diffraction curves for p-benzoquinone. The arrows on curve A are at the measured positions of the corresponding features adjusted by the factor q_A/q_{obs}. For all models C–H = 1.09 Å. and C=C = 1.34 Å.

$C_2C_1C_6$, deg.	C–C	C=O		$C_2C_1C_6$, deg.	C–C	C=O	
116	1.51	1.25	A	113	1.50	1.20	J
116	1.48	1.26	B	119	1.47	1.22	K
116	1.54	1.30	C	119	1.50	1.22	L
116	1.56	1.30	D	119	1.54	1.28	M
116	1.48	1.22	E	119	1.54	1.32	N
116	1.54	1.25	F	119	1.50	1.28	O
113	1.50	1.24	G	Visual curve			V
113	1.54	1.26	H	Radial distribution curve			R
113	1.47	1.20	I				

C=C and C–C/C=C, are shown graphically (Fig. 2), and a contour line has been drawn to enclose the region of acceptable models. The assumed value of 1.34 Å. for the C=C distance was readjusted for all models by the usual quantitative comparison, and the corresponding values are indicated on the contour line.

In a similar manner, two limiting contours were drawn for models having angles of 113 and 119°, respectively. None of these models is entirely satisfactory. Among the four curves shown for an angle of 113°, curve G is the best, but is only barely within the range of acceptability because the seventh minimum is so poorly resolved; a curve between G and H would be better. Among the five best 119° models, L is the only one within the limiting contour, and even here the ninth minimum is too shallow and there is no shoulder on the eleventh maximum.

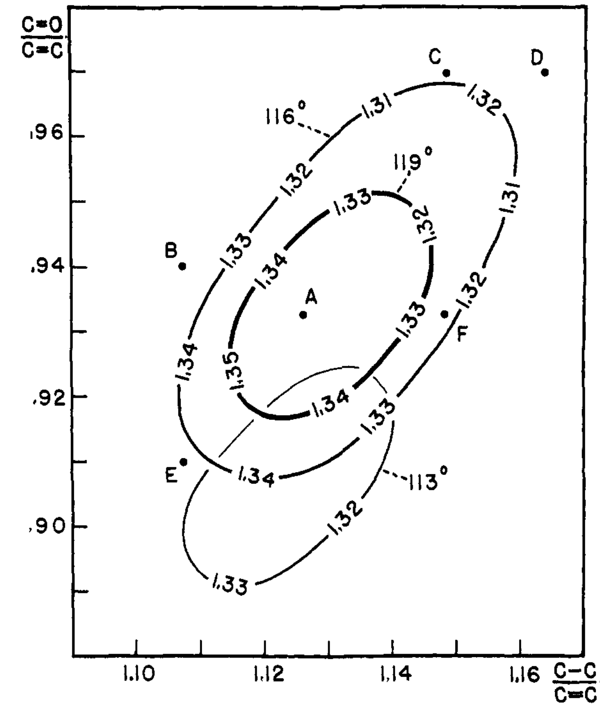


Fig. 2.—Contours showing limits of error in the bond length ratios of p-benzoquinone for three different bond angles. The values for C=C shown on the contours were obtained by multiplying the assumed value, 1.34 Å., by the ratio q/q_{obs}.

In addition to these uncertainties in the shape parameters, there is an uncertainty in the size parameter resulting from possible inaccuracy in the various physical measurements involved, and from uncertainty in the best manner to weight the values of $q/q_{obs.}$ in taking their average. Accumulated experience with substances giving comparable scattering, including substances with independently determined structures, indicates that $\pm 1\%$, which must be added to limits imposed by uncertainty in the shape parameters, is an appropriate value. Consideration of all these factors leads to the following parameters and the over-all limits of error: C=C = 1.32 ± 0.04 Å., C–C = 1.50 ± 0.04 Å., C=O = 1.23 ± 0.04 Å., and $\angle C_2C_1C_6$ = 116 ± 3°.

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