531. *The Heats of Combustion of Quinol and* p-*Benzoquinone and the Thermodynamic Quantities of the Oxidation–Reduction Reaction.*

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The heats of combustion at 25° and 1 atmosphere's pressure of *p*-benzoquinone and quinol have been found to be 656·29 ± 0·10 and 681·75 ± 0·21 kcal./mole, respectively; values for the corresponding heats of formation, 44·65 ± 0·17 and 87·51 ± 0·28 kcal./mole, respectively, have been derived. By making use of available specific-heat data, the free-energy change at constant pressure for the reduction of solid *p*-benzoquinone to quinol has been calculated to be 31·83 kcal./mole, compared with 31·43 obtained directly from redox-potential measurements. The corresponding thermodynamic quantities have been calculated for this reaction in solution and in the gaseous states. The heat-content changes are best derived from thermochemical measurements and the free-energy changes from electrochemical measurements.

THE reversible oxidation–reduction conversions of quinols into quinones are of great interest because the free-energy changes can be derived from measurements of the redox potentials. These have been made for a wide variety of quinone systems, mainly by Fieser and his co-workers.[1]

The free-energy change of a reaction at constant pressure is related to the heat content and entropy changes by $\Delta G = \Delta H - T\Delta S$. ΔG is related to the redox potential $E°$ by the relation $\Delta G = 2FE°$ ($F = 23068{\cdot}1$ cal./int.v/equiv.).[2] Values for ΔH and ΔS can be derived from the variation of ΔG with temperature. This has been done in several cases

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[1] Cf. Evans and de Heer, *Quart. Rev.*, 1950, **4**, 94.

[2] " Selected Values of Thermodynamic Properties," Nat. Bur. Stand. Circ. 500, 1952.

by Conant and Fieser,[3,4] but the values of ΔH so obtained are not accurate because the temperature range over which observations can be made is small. ΔH can also be obtained from the heats of formation of quinols and quinones; a series of such measurements was made by Valeur [5] but the results were of low precision.

It was deemed useful to examine critically the thermodynamic quantites for the *p*-benzoquinone–quinol system by making high-precision measurements of the heats of combustion. Such measurements were made by Schreiner [6] in 1925, and by Parks, Manchester, and Vaughan [7] in 1954 concurrently with and independently of the present work. The variations of specific heat with temperature for these compounds were reported by Lange [8] so an independent determination of ΔS is possible. These thermochemical results can be compared with the electrochemical ones, and a more accurate thermodynamic description of the reaction can then be made, so providing a more reliable basis for theoretical discussion.

EXPERIMENTAL

The high-precision aneroid calorimeter described by Pilcher and Sutton [9] was used. The technique and conditions were in general exactly as those given by them,[9] a " main-period " of 60 min. being used.

All combustions were done under 30 atm. pressure of oxygen and the air in the bomb was first swept out by twice filling to 15 atm. Water (1 ml.) was placed in the bomb, and a platinum covering shield was placed over the crucible to assist complete combustion. The substance, in pellet form, was weighed to about 5×10^{-6} g. The determination of the auxiliary energy quantities was made as before, *viz.*, those due to (i) ignition, (ii) nitric acid formation, and (iii) carbon residue formation. Analysis of the bomb gases for carbon dioxide was not attempted. We thought it better to test for carbon monoxide. This was done by Winkler's method [10] and, if the test was positive, the combustion value was rejected. All the weights of substances examined were corrected *ad vacuo*. The energy quantities are given in thermochemically defined calories,[2] and all errors quoted were calculated by Rossini's [11] method.

The apparatus was calibrated by benzoic acid combustions (B.D.H. Thermochemical Standard), and the calibration constant derived from an assumed value for its isothermal heat of combustion at 25° of 26,429·4 ± 2·6 int. J/g.(vac.) = 6317·84 cal./g.(vac.),[12] corrected for non-standard conditions as recommended by Jessup and Green.[13] The non-isothermal heat of combustion, where the temperature changes from 23·455° to 25·244°, was calculated by subtracting the isothermal correction.[14] The heat of combustion of benzoic acid under these conditions is 6317·10 cal./g.(vac.).

Fourteen calibrations were done as described in reference 9, and the result, expressed as calories divided by the corrected temperature rise in ohms, was $K = 8626{\cdot}59 \pm 0{\cdot}59$ (±0·007%). The standard deviation for a single experiment was 0·012%. The conditions were also varied to show that this calibration constant is applicable within the limits in which it is employed.

The results are given as the isothermal values at 25° and the Washburn corrections were applied, his notation [14] being used.

Quinol.—The first sample (I) was obtained by crystallising quinol (B.D.H. Laboratory Reagent) four times from ethanol, drying it *in vacuo* and heating it in air to 130° for 90 min. Sample II was obtained by crystallising quinol twice from ethanol and then once from distilled water in absence of air. It was dried as was sample I. The densities were checked to show that the modification used was α-quinol (*d*, 1·33 g./c.c.).

The results are shown in Table 1. The total heat quantity was obtained by multiplying the corrected temperature rise by the calibration constant K.

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[3] Conant and Fieser, *J. Amer. Chem. Soc.*, 1922, **44**, 2480.
[4] *Idem, ibid.*, 1923, **45**, 2194.
[5] Valeur, *Ann. Chim. Phys.*, 1900, **21**, 470.
[6] Schreiner, *Z. phys. Chem.*, 1925, **117**, 57.
[7] Parks, Manchester, and Vaughan, *J. Chem. Phys.*, 1954, **22**, 2089.
[8] Lange, *Z. phys. Chem.*, 1924, **110**, 351.
[9] Pilcher and Sutton, *Phil. Trans.*, 1955, *A*, **248**, 23.
[10] Winkler, *Z. analyt. Chem.*, 1935, **102**, 99.
[11] Rossini, *Chem. Rev.*, 1936, **18**, 233.
[12] Jessup, *J. Res. Nat. Bur. Stand.*, 1946, **36**, 421.
[13] Jessup and Green, *ibid.*, 1934, **13**, 469.
[14] Washburn, *ibid.*, 1933, **10**, 525.

TABLE 1.

Molecular weight ($C_6H_6O_2$) = 110·108. Isothermal correction = 0·31 cal.

Sample	Weight [g. (vac.)]	Total heat quantity (cal.)	Total ignition energy (cal.)	C * (cal.)	HNO_3 † (cal.)	$-\Delta U_B$ (isothermal) (kcal./mole)	Deviation from mean $-\Delta U_B$
I	0·508805	3164·25	13·24	1·23	0·80	682·05	0·00
I	0·510026	3170·58	12·98	1·75	0·65	681·99	0·06
I	0·510321	3174·43	13·07	0·68	1·02	682·10	0·05
					Mean	682·05	
II	0·510523	3173·08	12·96	1·39	0·80	681·76	0·10
II	0·508940	3164·75	13·33	0·99	0·65	681·94	0·08
II	0·508657	3161·76	13·05	1·62	0·58	681·89	0·03
					Mean	681·86	

* Energy correction due to carbon residue formation.
† Energy correction due to nitric acid formation, taken to be 13·97 kcal./mole, at constant volume and 25° (Becker and Roth [15]).

For the sample crystallised from ethanol, the result is,

$$-\Delta U_B = 682{\cdot}05 \pm 0{\cdot}06 \text{ kcal./mole } (\pm 0{\cdot}009\%)$$

and for the sample crystallised from water,

$$-\Delta U_B = 681{\cdot}86 \pm 0{\cdot}11 \text{ kcal./mole } (\pm 0{\cdot}016\%)$$

The difference, 0·028%, is probably due to retention of solvent. For equimolecular amounts retained, water would decrease the value more than ethanol would increase it, so the true result is probably nearer the higher value. We shall, however, take the mean value and increase the error accordingly, *i.e.*,

$$-\Delta U_B = 681{\cdot}96 \pm 0{\cdot}19 \text{ kcal./mole } (\pm 0{\cdot}028\%)$$

and by applying the Washburn corrections :

$$-\Delta U_R = 681{\cdot}45 \pm 0{\cdot}21 \text{ kcal./mole } (\pm 0{\cdot}03\%)$$

and $-\Delta H_R{}^\circ$, the heat of combustion at constant pressure under the standard conditions, is

$$-\Delta H_R{}^\circ = 681{\cdot}75 \pm 0{\cdot}21 \text{ kcal./mole}$$

The errors quoted for the $-\Delta U_B$ values are the precision errors of the measurements; those for $-\Delta U_R$ and $-\Delta H_R{}^\circ$ include the precision errors of the calibration and the uncertainty in the value for benzoic acid.

p-*Benzoquinone.*—Benzoquinone (B.D.H. Technical Grade) was crystallised from light petroleum (b. p. 60—80°) (charcoal) and then sublimed in air. Three samples were examined. Sample I was this material crystallised from light petroleum (b. p. 60—80°). (which had been shaken with concentrated sulphuric acid to remove unsaturated substances) and then resublimed in air. Sample I was resublimed to give sample II. Sample III was the starting material for sample I resublimed. The combustion results for these samples agree to within experimental error. As benzoquinone slowly decomposes, all samples were prepared not more than 12 hr. before combustion and kept away from light.

The loss of weight due to evaporation in transferring the pellet to the bomb was found to be negligible. As a small amount of benzoquinone evaporated into the bomb space before the ignition, the chance of obtaining complete combustion was enhanced by increasing the flame volume by not placing the platinum cover over the crucible; the cover was, however, placed in the bomb. Because of the high volatility of this compound, the air initially in the bomb was not swept out with oxygen, and consequently the nitric acid correction was greatly increased. There were no signs of incomplete combustion as shown by the carbon monoxide test. Furthermore the exit gases from the bomb were passed through concentrated sodium hydroxide solution and no colour was produced. The combustion results are given in Table 2. Previous values are collected in Table 3.

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[15] Becker and Roth, *Z. Elektrochem.*, 1934, **40**, 836.

TABLE 2.

Molecular weight ($C_6H_4O_2$) = 108·092. Isothermal correction = 0·29 cal.

Sample	Wt. [g. (vac.)]	Total heat quantity (cal.)	Total ignition energy (cal.)	C (cal.)	HNO_3 (cal.)	$-\Delta U_B$ (isothermal) (kcal./mole)	Deviation from mean $-\Delta U_B$
I	0·514241	3142·45	13·73	0·95	4·86	656·89	0·05
I	0·519364	3172·53	13·73	1·20	4·71	656·75	0·09
II	0·520628	3179·92	13·10	1·32	4·79	656·83	0·01
III	0·520470	3179·15	12·59	1·00	4·86	656·89	0·05
					Mean	656·84	

$$\begin{aligned} -\Delta U_B &= 656{\cdot}84 \pm 0{\cdot}06 \text{ kcal./mole } (\pm 0{\cdot}0009\%) \\ -\Delta U_R &= 656{\cdot}29 \pm 0{\cdot}10 \text{ kcal./mole } (\pm 0{\cdot}015\%) \\ -\Delta H_R{}^\circ &= 656{\cdot}29 \pm 0{\cdot}10 \text{ kcal./mole } (\pm 0{\cdot}015\%) \end{aligned}$$

TABLE 3. *Comparison with previous measurements.*

Quinol			*p*-Benzoquinone		
Authors	Year	$-\Delta H_R{}^\circ$ (kcal./mole)	Authors	Year	$\Delta H_R{}^\circ$ (kcal./mole)
Stohmann, Rodatz, and Herzberg [a]	1886	670·1	Berthelot and Recoura [e]	1888	659·5 ± 1
Berthelot and Lougninine [b]	1888	685·9 ± 3	Berthelot and Louguinine [b]	1888	655·2 ± 2
Stohmann and Langbein [c]	1892	683·3 ± 1	Valeur [d]	1900	658·0 ± 1
Valeur [d]	1900	683·7 ± 1	Schreiner [6]	1925	656·6 ± 0·2
Schreiner [6] *	1925	682·3 ± 0·2	Parks, Manchester, and Vaughan [7] †	1954	656·84 ± 0·28
Parks, Manchester, and Vaughan [7] †	1954	682·51 ± 0·28	This work	—	656·29 ± 0·10
This work	—	681·75 ± 0·21			

* Schreiner reported measurements on sublimed quinol which contains a third modification, γ-quinol, about which little is known.

† Although the difference between the values obtained for the individual substances by Parks *et al.*[7] and by the present authors is disconcertingly large, the quinol–benzoquinone differences obtained by both sets of authors are in satisfactory agreement, being 25·67 (Parks, Manchester, and Vaughan) and 25·46 (this work).

[a] *J. prakt. Chem.*, 1886, **33**, 467. [b] *Ann. Chim. Phys.*, 1888, **13**, 321. [c] *J. prakt. Chem.*, 1892, **45**, 305. [d] Valeur, ref. 5, corrected by Swietoslawski and Starczeska, *J. Chim. phys.*, 1925, **22**, 399. [e] *Ann. Chim. Phys.*, 1888, **13**, 298.

DISCUSSION

The reduction of benzoquinone (Q) to quinol (QH_2) can in principle be carried out with both species in the solid, solution, or gaseous state. The thermodynamic functions for these will be distinguished by superscripts, *e.g.*, $G^{(s)}$, $G^{(sol)}$, $G^{(g)}$ respectively.

(a) *The Oxidation–Reduction Reaction in the Solid State.*—$\Delta H^{(s)}$ is equal to the difference in heats of formation of benzoquinone and quinol referred to the standard states. These are calculated from the heats of combustion (this work) and the heats of formation of the products at 25°, the values $-\Delta H_f{}^\circ$ (CO_2) = 94·0518 ± 0·0108 and $-\Delta H_f{}^\circ$ (H_2O liq.) = 68·3174 ± 0·0096 kcal./mole. being used.[16] The appropriate values at 25° are :

$$-\Delta H_f{}^\circ (Q) = 44{\cdot}65 \pm 0{\cdot}17 ; \quad -\Delta H_f{}^\circ (QH_2) = 87{\cdot}51 \pm 0{\cdot}28 ;$$
$$-\Delta H^{(s)} = 42{\cdot}86 \pm 0{\cdot}25 \text{ kcal./mole}$$

The error in the last is the sum of the precision errors for the measurements of the heats of combustion of benzoquinone, quinol, and hydrogen, the uncertainty in the calibration being excluded.

$\Delta S^{(s)}$ is calculated from the difference in " absolute " entropy values (S°) at 25°. The specific heats of benzoquinone and quinol were measured from *ca.* 20° K to *ca.* 290° K by Lange.[8] Andrews[17] measured that of quinol between 110° K and 340° K. There is a slight difference between the results of the two workers, but Lange's results alone have been used because a difference in S° values is required. The entropies were computed by

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[16] Wagman, Kilpatrick, Taylor, Pitzer, and Rossini, *J. Res. Nat. Bur. Stand.*, 1945, **34**, 143.

[17] Andrews, *J. Amer. Chem. Soc.*, 1926, **48**, 1293.

the usual method,[18] it being assumed that there were no anomalies in the specific heat. The required entropy values are :

$$S^\circ\,(\mathrm{Q}) = 38{\cdot}55;\ S^\circ\,(\mathrm{QH_2}) = 32{\cdot}77;\ S^\circ\,(\mathrm{H_2}) = 31{\cdot}21 \text{ cal./deg./mole}$$

the value for hydrogen being taken from ref. 2. Consequently, $-\Delta S^{(s)} = 37{\cdot}99$ cal./deg./mole and hence at 25° $-\Delta G^{(s)} = 31{\cdot}83$ kcal./mole. This corresponds to a redox potential of 0·690 v; the measured value,[4] 0·681 ± 0·001 v, corresponds to $-\Delta G^{(s)} = 31{\cdot}43$ kcal./mole. The variation of $E^{\circ(s)}$ with temperature from 0° to 25° C was also examined by Conant and Fieser [4] and $-\Delta H^{(s)}$ found to be 41·3 kcal./mole (our value 42·86). The agreement between the $-\Delta G^{(s)}$ values from the two methods is good; but it is poorer for the $-\Delta H^{(s)}$, and because Conant and Fieser state that the variations of $E^{\circ(s)}$ with temperature may be in error up to 13%, the thermochemical value of $-\Delta H^{(s)}$ is preferred. It appears, however, that the electrochemical value for $-\Delta G^{(s)}$ is the more accurate one because the specific heats given by Lange show considerable scatter from the smooth curve and there is remarkable agreement between the measurements of Conant and Fieser and those of other workers (see ref. 3).

Thermochemical and electrochemical measurements are thus complementary and $\Delta S^{(s)}$ is better determined from them than from the specific-heat data at present available.

(b) *The Oxidation–Reduction Reaction in Solution.*—If it be assumed that benzoquinone and quinol behave as ideal solutes, $E^{\circ(\mathrm{sol})}$ is related to $E^{\circ(s)}$ by : $E^{\circ(\mathrm{sol})} = E^{\circ(s)} - \dfrac{\boldsymbol{R}T}{2\boldsymbol{F}} \ln \dfrac{C_{\mathrm{Q}}^{(\mathrm{sat})}}{C_{\mathrm{QH_2}}^{(\mathrm{sat})}}$ (ref. 3) where $C_{\mathrm{Q}}^{(\mathrm{sat})}$ and $C_{\mathrm{QH_2}}^{(\mathrm{sat})}$ are the concentrations of benzoquinone and quinol in their respective saturated solutions. The solubilities were measured by Granger and Nelson.[19] The values of $E^{\circ(\mathrm{sol})}$ calculated from $E^{\circ(s)}$ and the solubility data, compared with the measured values shown in parentheses are: in 0·1N-hydrochloric acid 0·702 v (0·699 v); in N-hydrochloric acid 0·698 v (0·696 v).

The heats of solution in water of benzoquinone and quinol were measured by Berthelot and Werner [20] as 3·99 and 4·40 respectively and by Schreiner [6] as 4·69 and 4·48 kcal./mole respectively. The value of 4·45 kcal./mole for quinol was obtained by Kolossowsky and Kraef.[21] Schreiner's values are preferred because directly comparative measurements were made. He also showed that the heats of solution of benzoquinone and quinol in dilute hydrochloric acid solution are not significantly different from these values; whence from $-\Delta H^{(s)}$ (thermochemical), $-\Delta H^{(\mathrm{sol})} = 43{\cdot}07$ kcal./mole. The electrochemical value obtained [3] from measurements of $E^{\circ(\mathrm{sol})}$ at several temperatures, in dilute hydrochloric acid solution, is 42·50 kcal./mole. $\Delta S^{(\mathrm{sol})}$ is determined from $\Delta G^{(\mathrm{sol})}$ (electrochemical) and $\Delta H^{(\mathrm{sol})}$ (thermochemical).

(c) *The Oxidation–Reduction Reaction in the Gaseous State.*—If it be assumed that the vapours of benzoquinone and quinol behave as ideal gases at 25°, $E^{\circ(g)}$ is related to $E^{\circ(s)}$ by : $E^{\circ(g)} = E^{\circ(s)} - \dfrac{\boldsymbol{R}T}{2\boldsymbol{F}} \ln \dfrac{P_{\mathrm{Q}}}{P_{\mathrm{QH_2}}}$ where P_{Q} and $P_{\mathrm{QH_2}}$ are the vapour pressures at 25° (see Conant [22]). $E^{\circ(g)}$ has not been measured directly.

There are several reported values for the vapour pressures and heats of vaporisation of benzoquinone and quinol. Those of Coolidge and Coolidge [23] are without clear significance because the plots of log P against $1/T$ are not linear. Wolf and Trieschmann [24] give $\Delta H^{v}\,(\mathrm{QH_2}) = 23{\cdot}7 \pm 0{\cdot}4$ kcal./mole but give no experimental details. The most reliable determination appears to be that due to Nitta *et al.*[25] who obtained at 25° : benzoquinone, $\Delta H^{v} = 16{\cdot}38$ kcal./mole, $\Delta S^{v} = 38{\cdot}1$ cal./deg./mole : quinol, $\Delta H^{v} = 21{\cdot}54$ kcal./mole, $\Delta S^{v} = 38{\cdot}0$ cal./deg./mole. The values of P_{Q} and $P_{\mathrm{QH_2}}$ thence calculated for

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[18] Lewis and Randall, " Thermodynamics," McGraw-Hill, New York, 1923.
[19] Granger and Nelson, *J. Amer. Chem. Soc.*, 1921, **43**, 1401.
[20] Berthelot and Werner, *Ann. Chim. Phys.*, 1886, **7**, 103.
[21] Kolossowsky and Kraef, *J. Chim. phys.*, 1925, **22**, 94.
[22] Conant, *J. Amer. Chem. Soc.*, 1927, **49**, 293.
[23] Coolidge and Coolidge, *J. Amer. Chem. Soc.*, 1927, **49**, 100.
[24] Wolf and Trieschmann, *Z. phys. Chem.*, 1934, *B*, **27**, 376.
[25] Nitta, Seki, Chihara, and Suzuki, *Sci. Reports Osaka Univ.*, 1951, No. 29.

25° being used, with Conant and Fieser's[4] for $E^{\circ(s)}$, then $E^{\circ(g)} = 0{\cdot}570$ v and $-\Delta G^{(g)} = 26{\cdot}30$ kcal./mole. $-\Delta H^{(g)}$ is calculated from $-\Delta H^{(s)}$ and the difference in heats of vaporisation to be 37·70 kcal./mole. $\Delta S^{(g)}$ is obtained from $-\Delta G^{(g)}$ and $-\Delta H^{(g)}$.

The values thus calculated of the thermodynamic quantities describing this reaction in the various states are as follows :

	$-\Delta H$ (kcal./mole)	$-\Delta G$ (kcal./mole)	ΔS (cal./deg./mole)
Solid	42·86 ± 0·25	31·43 ± 0·05	37·0 ± 1·0
Solution : 0·1N-HCl	42·45 ± 0·50	32·25 ± 0·05	34·2 ± 1·2
1·0N-HCl	42·45 ± 0·50	32·11 ± 0·05	34·7 ± 1·2
Gas	37·70	26·30	38·2

It is not possible to assess the errors for the quantities relating to the gaseous state with any certainty.

Theoretical Discussion.—The first important theoretical suggestion concerning these reactions, made by Branch and Calvin,[26] was that the " driving force " was due to the gain in resonance energy of the quinol over the benzoquinone. This is the basis of further theoretical calculations by Evans,[27] Diatkina and Syrkin,[28] and Evans, Gergely, and de Heer,[29] which have been reviewed by Evans and de Heer.[1]

These theoretical calculations purport to give the difference in energy of the corresponding quinols and quinones as isolated molecules. The results should be compared therefore with values of $-\Delta U^{(g)}$ or, since $\Delta U^{(g)}$ and $\Delta H^{(g)}$ differ by a constant amount for all such pairs, $-\Delta H^{(g)}$. These thermodynamic quantities are not known with much accuracy save for the *p*-benzoquinone–quinol system.

What has in fact been done is to compare either a theoretical or an empirical resonance energy difference (for the latter see Berliner[30]) with the free energy $-\Delta G^{(sol)}$ obtained from the redox potentials. Approximate linear relationships have been found although the significance thereof is not clear, as Branch and Calvin clearly stated. The free-energy change in the gas phase is related to that in solution as follows :

$$\begin{aligned}\Delta G^{(sol)} &= \Delta G^{(g)} + \Delta G_{QH_2}{}^{(solvation)} - \Delta G_{Q}{}^{(solvation)} \\ &= [\Delta H^{(g)} + \Delta H_{QH_2}{}^{(solvation)} - \Delta H_{Q}{}^{(solvation)}] - T[\Delta S^{(g)} + \Delta S_{QH_2}{}^{(solvation)} - \Delta S_{Q}{}^{(solvation)}]\end{aligned}$$

The $\Delta H^{(solvation)}$ values, which are each the algebraic sum of the heats of vaporisation and of solution of the solid, are themselves of the same order of magnitude as $\Delta H^{(g)}$. Furthermore it is hardly to be expected that the entropy terms remain constant throughout the complete series. For these reasons, the existence of a linear relation between $\Delta G^{(sol)}$ and the estimated resonance energy which should be related to $\Delta H^{(g)}$, is surprising. Conant[22] found that the values of $\Delta G^{(sol)}$ for *p*-benzoquinones were an irregular function of the degree of substitution by chlorine, whereas the $\Delta G^{(g)}$ values were regular.

It appears, therefore, that for the better understanding of the factors determining the free-energy changes in this series, improvements in the calculation of resonance-energy changes are at present less necessary than are accurate thermochemical measurements.

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[26] Branch and Calvin, " The Theory of Organic Chemistry," Prentice-Hall, New York, 1941.
[27] Evans, *Trans. Faraday Soc.*, 1946, **42**, 113.
[28] Diatkina and Syrkin, *Acta Physicochim. U.R.S.S.*, 1946, **21**, 921.
[29] Evans, Gergely, and de Heer, *Trans. Faraday Soc.*, 1949, **45**, 312.
[30] Berliner, *J. Amer. Chem. Soc.*, 1946, **68**, 49.