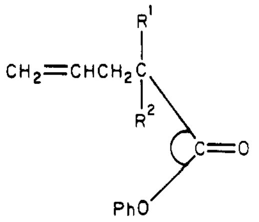
During the vibration of the carbonyl bond both atoms move with almost equal amplitudes. For accommodation of the movement of the carbon atom some compression or deformation of the adjacent C–C or C–O bonds must take place. A coupling effect then comes into play, which can lead to a change of the carbonyl frequencies without any corresponding change in the carbonyl force constant. Bellamy[12] suggests that the greater part of the observed changes of the carbonyl frequencies with ring size originate in coupling effects of the type discussed above. Similarly, the low carbonyl frequencies shown by di-*tert*-butyl ketone and by α-substituted methyl aryl ketones are due primarily to increases in the C–C–C bond angles.[13]

We suggest, then, that the shifts of IR bands to lower frequency observed for the carbonyl group when hydrogen atoms of the α-carbon in allylacetate are substituted by alkyl or phenyl groups are due to a change in the carbonyl group valency angle as shown below.



Registry No. Allylethylacetic acid, 1575-73-1; allylisopropylacetic acid, 1575-71-9; methylphenylacetic acid, 492-37-5; allylmethylphenylacetic acid, 76403-17-3; allyldimethylacetic acid, 16386-93-9; phenyl allylethylacetate, 80765-41-9; phenyl allylisopropylacetate, 80765-42-0; phenyl allylmethylphenylacetate, 80765-43-1; phenyl allyldimethylacetate, 80765-44-2; phenyl acetate, 122-79-2; phenyl allylacetate, 51231-09-5; phenyl allylphenylacetate, 51231-03-9; phenyl allyldiphenylacetate, 51231-12-0; phenyl trimethylacetate, 4920-92-7.

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(12) L. J. Bellamy, "Advances in Infrared Group Frequencies", Methuen & Co. Ltd., London, 1969, Chapter 5.

(13) J. A. Adelfang, P. H. Hess, and N. H. Cronwell, *J. Org. Chem.*, **26**, 1402 (1961).

(14) M. Moura Campos and L. do Amaral, *Arch. Pharm. (Weinheim, Ger.)*, **298**, 92 (1965).

(15) E. E. Eliel and J. P. Freeman, *J. Am. Chem. Soc.*, **74**, 927 (1952).

(16) K. C. Brannock, H. S. Pridgen, and B. Thompson, *J. Org. Chem.*, **25**, 1815 (1960).

Notes

2-(2-Methyl-3-indolyl)-1,4-benzoquinone, a Reversible Redox Substrate at the Carbon-Paste Electrode in Acidic Aqueous–Ethanolic Media

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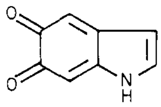
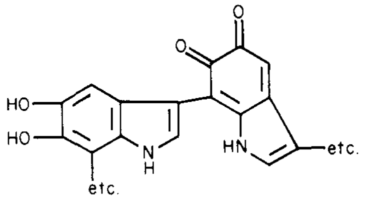
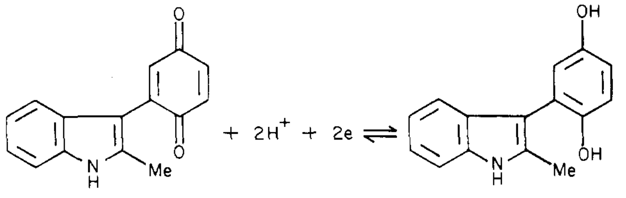
The oxidative polymerization of dopa (3,4-dihydroxyphenylalanine) to the mammalian pigment melanin has long been considered to proceed via a pathway involving a series of fugitive quinonoid intermediates,[1] of which indole-5,6-dione (1) was first postulated as the principal building block of the polymeric pigment.[2] Since model studies[3] had demonstrated that indoles readily react with simple *o*- and *p*-quinones to yield indolyl quinones (such as **3** from 2-methylindole and *p*-benzoquinone), it was considered likely that **1** would condense with its reduced form, 5,6-dihydroxyindole (DHI), to yield a dimeric species, which on further repetitive oxidation and addition would yield a polymer having a structure of type **2** (or variant involving other modes of ring–ring coupling) as a primary repeating unit. Although melanin is now considered to be a variegated polymer, comprising structural contributions from each of several precursors,[4] the dominant redox structure of the pigment is still believed to be an indolyl quinone moiety. For these reasons, and as part of our ongoing electrochemical studies of the melanization reactions of dopa[5] and its analogues,[6] it became of interest to examine the redox behavior of 2-(2-methyl-3-indolyl)-1,4-benzoquinone (**3**) as an easily accessible, prototypical indolyl quinone system.



1



2



3 **4**

Cyclic voltammetry of 0.211 mM 2-(2-methyl-3-indolyl)-1,4-benzoquinone (**3**) in the mixed solvent 1 M perchloric acid/95% ethanol (4:1, v/v) of apparent pH 0.60 at 25 °C showed that the system (**3** ⇌ **4**) is essentially reversible at the carbon-paste electrode. Within the potential window from +0.7 to 0.0 V (SCE) and at a scan rate of 0.050 V/s the cyclic voltammogram, initiated from +0.07 V toward more negative potentials, exhibited a cathodic peak at $E_{pc} = +0.460$ V for the reduction (**3** → **4**) and an anodic peak $E_{pa} = +0.490$ V for the oxidation (**4** → **3**). The peak separation, $E_{pa} - E_{pc} = 0.030$ V, is comparable with that expected (0.029 V) for a reversible two-electron transfer,[7] and, in corroboration, the cathodic half-peak

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(1) Nicolaus, R. A. "Melanins"; Hermann: Paris, 1968.

(2) Mason, H. S. *J. Biol. Chem.* **1948**, *172*, 83.

(3) Bu'Lock, J. D.; Harley-Mason, J. *J. Chem. Soc.* **1951**, 703.

(4) Swan, G. A.; Waggott, A. *J. Chem. Soc. C* **1970**, 1409. King, J. A. G.; Percival, A.; Robson, N. C.; Swan, G. A. *Ibid.* **1970**, 1418.

(5) Young, T. E.; Griswold, J. R.; Hulbert, M. H. *J. Org. Chem.* **1974**, *39*, 1980.

(6) Young, T. E.; Babbitt, B. W.; Wolfe, L. A. *J. Org. Chem.* **1980**, *45*, 2899.

0022-3263/82/1947-1571$01.25/0

potential also occurred at 0.490 V.

Measurement of the cathodic peak current (i_{pc}) and the anodic peak current (i_{pa}), the latter by the potential-hold method delineated by Adams,[7] gave an anodic to cathodic peak current ratio of unity (observed: $i_{pa}/i_{pc} = 1.00 \pm 0.02$) as expected theoretically. Furthermore, the peak cathodic current calculated[7,8] for a reversible two-electron transfer, using a diffusion coefficient derived from chronoamperometric data (vide infra), was $i_{pc} = 23.5$ μA in good agreement with the observed value of 23.8 μA. On the basis of this overall assessment of reversibility, the half-wave potential, taken at 85% of the cathodic peak current,[8] was $E_{1/2} = +0.47$ V in this solvent system.

In solvent media composed of McIlvaine buffers/95% ethanol (4:1, v/v) the redox process became increasingly irreversible with increasing pH as indicated by the anodic to cathodic peak separation ($\Delta E_p = 0.098$ V at pH 2.27 and $\Delta E_p = 0.367$ V at pH 7.15). Despite this, the cathodic half-peak potential was linear with pH and followed the equation $E_{pc/2} = 0.432 - 0.067$ pH (correlation coefficient = 0.983) in the pH range 2.27–7.15.

Although the redox process observed for 2-(2-methyl-3-indolyl)-1,4-benzoquinone (**3** $\rightleftharpoons$ **4**) in the perchloric acid medium was a simple, reversible charge transfer, more complex behavior was observed by widening the potential window to +1.100 V and initiating the cyclic voltammogram at +0.70 V and then scanning toward more positive potentials. Under these conditions (and at a scan rate of 0.050 V/s) a totally irreversible oxidative wave was observed at $E_{pa} = +1.00$ V, with no companion cathodic wave on scan reversal. The remaining part of the scan showed the reversible couple (**3** $\rightleftharpoons$ **4**) as described previously. The anodic wave at 1.00 V probably involved oxidation of the indole moiety since in separate control experiments both 2-methylindole ($E_{pa} = 1.05$ V at pH 0.60) and indole ($E_{pa} = 0.900$ V at pH 6.8)[9,10] exhibited totally irreversible waves in the same region. The nature of this oxidation is, however, not interpretable at this time since the anodic electrochemical behavior of simple indoles is complex and not well understood.[11]

Chronoamperometry experiments were performed on 2-(2-methyl-3-indolyl)-1,4-benzoquinone (**3**) at four concentrations (0.100, 0.140, 0.180, and 0.200 mM), each at seven different acidities covering the pH range from 0.60 to 7.15. The data array (at 25 °C) yielded an average $it^{1/2}/C = 78.8 \pm 2.2$ (± standard error) from which the diffusion coefficient, $D = (0.38 \pm 0.02)10^{-5}$ cm^2/s, was calculated from the Cottrell equation. This value of D appeared to be reasonable compared with the few known values of diffusion coefficients for other organic molecules determined in dominantly aqueous media.[12]

Overall, the cathodic reduction of 2-(2-methyl-3-indolyl)-1,4-benzoquinone (**3**) at the Nujol–carbon-paste electrode is remarkably well-behaved in strongly acidic media, and its reversibility is comparable with that observed on anodic oxidation of *o*-dianisidine.[12] At higher pH values the indolyl quinone **3** is more nearly comparable with the *p*-quinone–hydroquinone system, which is notably irreversible at solid electrodes.[13,14] The indolyl *p*-quinone **3**, and perhaps other *o*-quinonoid analogues, may be of further value as reactivity models of low-molecular-weight oligomeric quinones which occur as transient intermediates during melanization reactions.

Experimental Section

2-(2-Methyl-3-indolyl)-1,4-benzoquinone (3). This compound was prepared from 2-methylindole and *p*-benzoquinone as described in the literature,[3,15] and recrystallized from 95% ethanol as deep violet crystals, mp 181–182 °C (lit.[15] mp ca. 185 °C).

Electrochemistry. These experiments were done on a Princeton Applied Research system comprising a Model 175 programmer, a Model 173 potentioistat with Model 176 I/E converter, and Model 178 electrometer probe. The carbon paste in the working electrode was formulated from Nujol and purified graphite (Matheson, Coleman, and Bell), using standard procedures.[14] Potentials were recorded vs. a saturated calomel electrode. The area of the working electrode was calibrated (0.37 cm^2) by chronoamperometry, using *o*-dianisidine in 1.02 M sulfuric acid, for which a reference diffusion coefficient was taken as $D = 0.44 \times 10^{-5}$ cm^2/s.[12] Cyclic Voltammograms were recorded up to 0.200 V/s on a Houston Model 2100-4-5 X–Y recorder, and faster scans up to 5.0 V/s were observed and recorded photographically on a Tektronix Model 5103N storage oscilloscope. Chronoamperometry experiments were recorded on the same equipment, using the time base of the X–Y recorder. Jacketted electrochemical cells were maintained at constant temperature via water circulating from a thermostatic bath maintained internally at 25 ± 0.04 °C.

The perchloric acid solutions consisted of 1 M perchloric acid/95% ethanol in a 4:1 volume ratio (pH 0.60). Various buffer solutions were prepared from standard 1 M ionic strength McIlvaine buffers/95% ethanol in a 4:1 volume ratio. All pH values were those of the mixtures. The partially ethanolic solutions were necessary to dissolve the substrate molecule (**3**).

Acknowledgment. We are grateful to the National Institutes of Health for Grant NS 12608 from NINCDS for support of this work.

Registry No. 3, 80641-49-2; **4**, 80641-50-5; 2-methylindole, 95-20-5; *p*-benzoquinone, 106-51-4.

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[7] Adams, R. N. "Electrochemistry at Solid Electrodes"; Marcel Dekker: New York, 1969; Chapter 5.

[8] Nicholson, R. S.; Shain, I. *Anal. Chem.* **1964**, *36*, 706.

[9] It should be noted that while 2-methylindole is stable in acidic media, indole itself dimerizes readily[10] and could not be run in the perchloric acid solution.

[10] Remers, W. A. In "Indoles"; Houlihan, W. J. Ed.; Wiley-Interscience: New York, 1972; Part 1, pp 66–67.

[11] Cheek, G. T.; Nelson, R. F. *J. Org. Chem.* **1978**, *43*, 1230.

[12] Reference 7, pp 221–222.

[13] Reference 7, pp 365–367.

[14] Lindquist, *J. Electroanal. Chem. Interfacial Electrochem.* **1974**, *52*, 37.

[15] Mohlau, R.; Redlich, A *Ber. Dtsch. Chem. Ges.* **1911**, *44*, 3605.

Kinetic Study of the Isomerization of Itaconic Anhydride to Citraconic Anhydride

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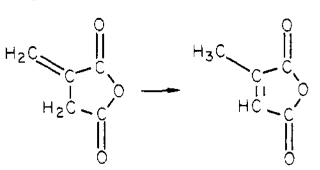
It is known that direct heating,[1] either via distillation or simple melting, isomerizes itaconic anhydride (ITA, **1**)



1 **2**

to citraconic anhydride (CTA, **2**). Using a spectrophotometric technique, Barb[2] showed that the isomerization of

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[1] Blatt, A. H. "Organic Syntheses"; Wiley: New York, 1943; Collect Vol. II, p 140.