

di- $\pi$ -methane reaction in which both the present data and such insights become crucial will be reported separately.<sup>52</sup>

### Summary

We have improved the technique of time-resolved photoacoustic calorimetry and have used it to determine the relaxed energies and lifetimes of a series of olefin triplets. Compounds with transient lifetimes as short as 20 ns can be resolved. The time-resolved photoacoustic calorimetry is a quick and reliable technique for determination of the relaxed transient energy. Results indicate

that acyclic olefin triplets are well described by the "1,2-biradical" structure.

**Acknowledgment.** We thank Professor Kevin S. Peters for providing exemplary software, advice, and assistance at the outset of this work. This work was supported by the National Science Foundation (Grant CHE-8516534) and the Robert A. Welch Foundation. Kinetic absorption spectroscopy was performed at the Center for Fast Kinetic Research at The University of Texas at Austin, supported by NIH Grant RR-00886 from the Biotechnology Branch of the Division of Research Resources and by The University of Texas. We thank Dr. S. C. Gupta for the sample of 1,1-diphenyl-1-butene.

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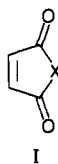
## Electron Affinities of Cyclic Unsaturated Dicarboxyls: Maleic Anhydrides, Maleimides, and Cyclopentenedione

Gary Paul and Paul Kebarle\*

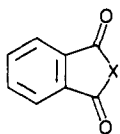
Contribution from the Chemistry Department, University of Alberta, Edmonton, Alberta, Canada T6G 2G2. Received July 18, 1988

**Abstract:** The electron affinities of 20 cyclic diones, mostly substituted maleic and phthalic anhydrides and maleimides and phthalimides, were determined by measuring gas-phase electron-transfer equilibria involving these compounds and reference compounds whose electron affinities were determined previously. A pulsed high pressure mass spectrometer (PHPMS) was used. The substituent effects for the anhydrides are similar to those observed earlier for the benzo- and naphthoquinones but somewhat larger. Comparison with the reduction potentials in solution permits the evaluation of the solvation energies of the radical anions in dimethylformamide. Significant decreases of solvation exothermicity with increasing electron affinities of the precursor neutral compounds are observed.

It has been known for some time that the cyclic unsaturated dicarbonyl compounds of structures I and II can capture electrons and form stable radical anions.<sup>1-4</sup> In particular the maleic an-



I



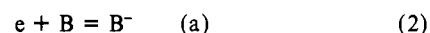
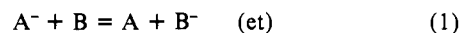
II

X = (O, NH, CH<sub>2</sub>)

hydride (I, X = O), phthalic anhydride (II, X = O), maleimide (I, X = NH) and phthalimide (II, X = NH) radical anions are known to form by one-electron reductions of the neutral parent compounds in solution.<sup>1,2</sup> Also in the gas phase, long-lived negative ions have been observed,<sup>4</sup> and some electron affinities have been determined. Compounds I and II resemble the benzo- and naphthoquinones with regard to electron capture. Thus, they also act as similar electron acceptors in charge-transfer complexes and also, but to a much lesser extent, have biological significance as electron carriers.<sup>5</sup>

Recently, we reported the determination of a large number of electron affinities<sup>6,7</sup> which were obtained by measuring elec-

tron-transfer (et) equilibria, see reaction 1, in the gas phase with



$$\Delta G^\circ = -RT \ln K \quad (3)$$

$$-\Delta H_a^\circ(B) \approx EA(B) \quad (4)$$

a pulsed electron high pressure mass spectrometer (PHPMS).<sup>8</sup> The  $\Delta G_1^\circ$  and  $\Delta H_1^\circ$  values obtained by making measurements with a number of compounds can be combined into a scale of relative electron attachment free energies  $\Delta G_a^\circ$  and  $\Delta H_a^\circ$ , see eq 2. By calibrating the scale to the literature value for  $\Delta G_a^\circ$  and  $\Delta H_a^\circ$  of one compound (SO<sub>2</sub>, primary standard), the rest of the absolute values are obtained.<sup>6</sup> In general, the structures and internal motions of B and B<sup>-</sup> are very similar, which leads to very similar heat capacities  $c_p(B)$  and  $c_p(B^-)$ . As a consequence, the electron affinity, which relates to electron attachment at 0 K, and the enthalpy change  $\Delta H_a^\circ$ , at 298 K, are numerically very similar such that  $EA \approx -\Delta H_a^\circ$  within 1-2 kcal/mol. Thus, not only  $\Delta G_a^\circ$  and  $\Delta H_a^\circ$  values are obtained but also fairly accurate EA. The  $\Delta G_a^\circ$  and the  $\Delta H_a^\circ$  are of interest in their own right, since in many actual experimental situations (thermal energies) it is these quantities and not the EA that are relevant.

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
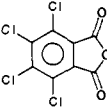

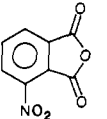

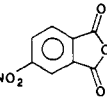




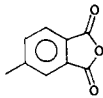






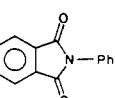


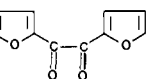
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Table I. Thermochemical Data for Electron Attachment:  $e + B = B^-$ 

B	$-\Delta G_a^\circ$ <sup>a</sup>		$-\Delta S_a^\circ$ <sup>b</sup>	$-\Delta H_a^\circ$ <sup>c</sup>	EA <sup>d</sup> lit.	B	$-\Delta G_a^\circ$ <sup>a</sup>		$-\Delta S_a^\circ$ <sup>b</sup>	$-\Delta H_a^\circ$ <sup>c</sup>	EA <sup>d</sup> lit.
	26.2	1.14	2	26.8	1.16		43.8	1.90	(3)	45.1	1.95, 1.7 <sup>g</sup> 1.6 <sup>h</sup>
	29.5	1.28	(1)	29.9	1.29		46.0	1.99	(3)	47.3	2.05
	32.8 (32.7) <sup>f</sup>	1.42	1	33.2	1.44, 1.4 <sup>e</sup> 1.4, <sup>f</sup> 1.3, <sup>g</sup> 1.6 <sup>h</sup>		47.8	2.07	(3)	49.1	2.13
	38.9	1.69	(3)	40.2	1.78		25.3	1.10	(1)	25.7	1.12
	43.5	1.89	(1)	43.9	1.90		25.5	1.11	(1)	25.9	1.12
	26.1	1.13	(3)	27.4	1.19		26.2	1.14	1	26.6	1.16
	26.8	1.16	(3)	28.1	1.22		30.0	1.30	3	31.4	1.36
	27.4 (27.4) <sup>f</sup>	1.19	3	28.7	1.24, 1.20 <sup>f</sup> 1.3, <sup>g</sup> 1.2 <sup>h</sup>		22.1	0.96	(3)	23.4	1.01
	30.7	1.33	(3)	32.0	1.39, 1.3 <sup>g</sup>		25.4	1.10	(3)	26.6	1.16
	37.2	1.61	(3)	38.5	1.67		25.8	1.12	(1)	26.2	1.14
							30.6	1.33	(1)	31.0	1.34

<sup>a</sup> $\Delta G_a^\circ$  at 423 K in kcal/mol. Estimated error  $\pm 1$  kcal/mol, values in eV also given, from Figure 1. <sup>b</sup> $\Delta S_a^\circ$  in cal/degree-mol. From van't Hoff plots Figures 2 and 4. Estimated values in brackets. Estimated error  $\pm 3$  cal/degree-mol. <sup>c</sup> $\Delta H_a^\circ$  in kcal/mol. From van't Hoff plots Figures 2 and 3 or from estimated  $\Delta S_a^\circ$ , see  $\Delta S_a^\circ$  in brackets. Estimated error  $\pm 2$  kcal/mol. <sup>d</sup>EA in eV from assumption  $-\Delta H_a^\circ = EA$ . <sup>e</sup>Compton et al.<sup>3</sup> from endothermic charge-transfer threshold. <sup>f</sup>Fukuda and McIver<sup>10</sup> (ICR). <sup>g</sup>Chen and Wentworth<sup>11</sup> charge-transfer spectra in solution,  $E_{CT}$ . <sup>h</sup>Chen and Wentworth<sup>11</sup> reduction potential in solution  $E_{1/2}$ .

After the determination of  $\Delta G_a^\circ$ ,  $\Delta H_a^\circ$ , and EA for the quinones,<sup>7</sup> it was natural to extend the measurements to the cyclic dicarboxyls, and these determinations are reported and discussed in the present work.

### Experimental Section

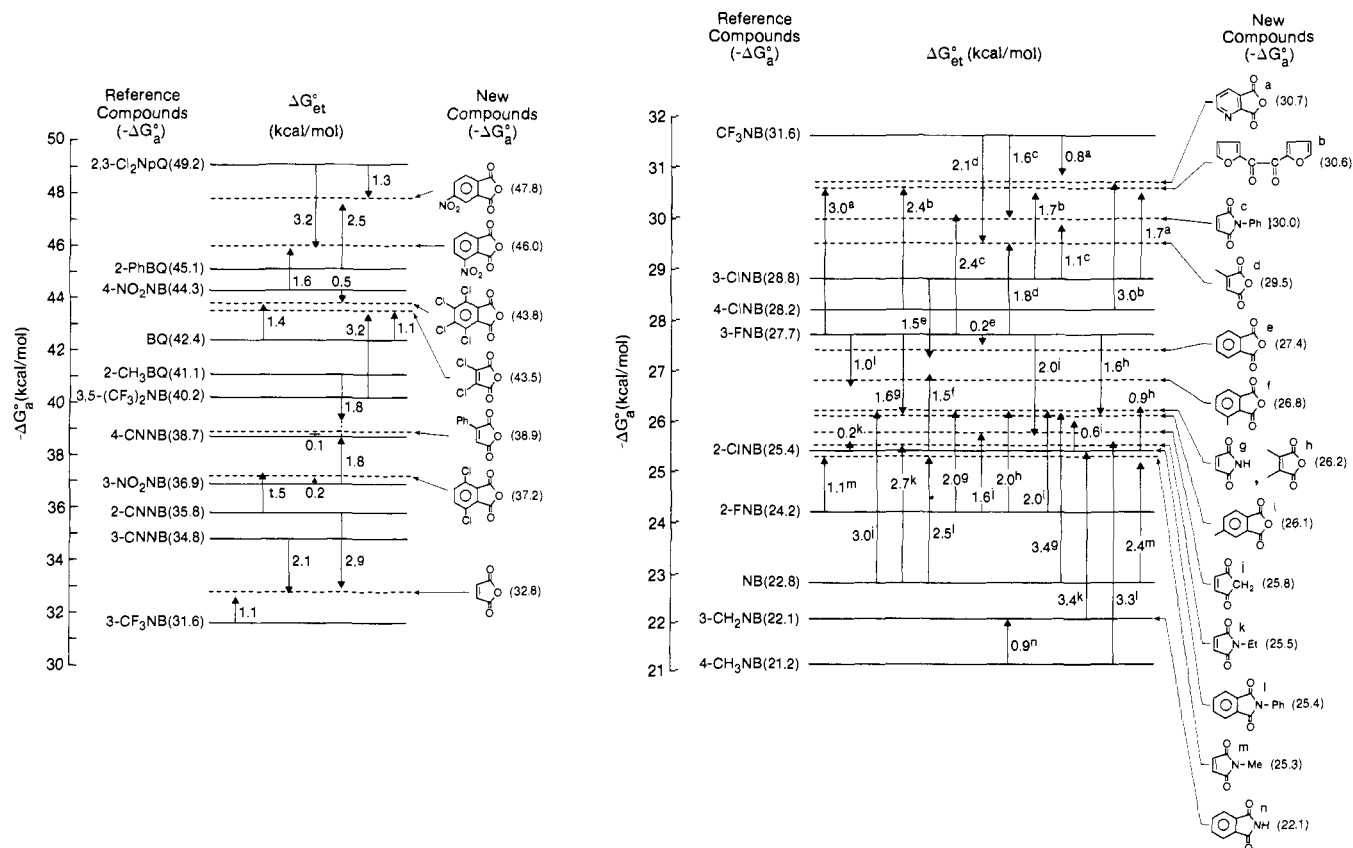
The measurements of the electron transfer equilibria (1) were performed with a pulsed electron high pressure mass spectrometer PHPMS. The apparatus and method have been described previously.<sup>6-8</sup> The measurements involving the present compounds were most similar to those previously described in the quinones<sup>7</sup> investigation. All the compounds used were obtained from commercial sources.

### Results and Discussion

**a. Thermochemical Data for Electron Attachment.** The equilibrium constants  $K_{et}$  of the electron-transfer reactions (1) determined at 423 K were used to evaluate  $\Delta G_{et}^\circ = -RT \ln K_{et}$ . The resulting  $\Delta G_{et}^\circ$  values are shown in Figure 1, combined in a scale of gradually increasing electron attachment free energies,  $\Delta G_a^\circ$ . The scale contains a number of reference compounds,

mostly substituted quinones and nitrobenzenes, whose  $\Delta G_a^\circ$ , see eq 2, were determined in previous work,<sup>6,7</sup> and the present relative values, i.e., the  $\Delta G_{et}^\circ$ , were used to obtain absolute values,  $\Delta G_a^\circ$ , for the new compounds by calibrating to the reference compounds, see Figure 1. For most of the new compounds, electron-transfer equilibria with two or more reference compounds were measured, and the resulting multiple thermodynamic cycles, see Figure 1, are seen to be consistent within less than 0.3 kcal/mol.

The  $\Delta G_a^\circ$  at 423 K for the 21 compounds of structures I and II obtained from Figure 1 are given in Table I. For a more limited number of compounds determinations of the equilibrium constants  $K_{et}$  at different temperatures were performed also. The resulting van't Hoff plots are shown in Figure 2. The  $\Delta H_{et}^\circ$  and  $\Delta S_{et}^\circ$  obtained from the slopes and the intercepts of the plots were used to construct the  $\Delta H_{et}^\circ$  and  $\Delta S_{et}^\circ$  scales shown in Figures 3 and 4. The consistency in the multiple  $\Delta H_{et}^\circ$  determinations is somewhat less satisfactory ( $\sim 0.5$  kcal/mol) than that observed in the  $\Delta G_{et}^\circ$  scale, Figure 1. The largest relative inconsistencies,  $\sim 2$  cal/deg mol, are seen in the  $\Delta S_{et}^\circ$  scale, Figure 4. It should



**Figure 1.** Values for electron transfer free energies  $\Delta G_{et}^\circ$  measured at 423 K. On the left side are reference compounds whose electron attachment free energies  $\Delta G_a^\circ$  for the process  $e + B = B^-$  were determined in earlier work.<sup>6,7</sup> Lengths of arrows correspond to given  $\Delta G_{et}^\circ$ .  $\Delta G_a^\circ$  deduced for new compounds are given in brackets in right column.

be noted that the  $\Delta H_a^\circ$  and  $\Delta S_a^\circ$  of the reference compounds are also uncertain to 1–2 kcal/mol and to  $\sim 2$  cal/deg<sup>6,7,9</sup> so that an error of  $\pm 2$  kcal/mol should be assumed for the  $\Delta H_a^\circ$  values and  $\pm 3$  cal/deg mol for the  $\Delta S_a^\circ$  values.

The  $\Delta S_a^\circ$  of the compounds for which van't Hoff plots were not obtained were estimated on the basis of  $\Delta S_a^\circ$  determined for compounds of similar structure. For these compounds the errors in  $\Delta H_a^\circ$  and  $\Delta S_a^\circ$  are even larger, and if one is interested in consistent comparisons between the compounds, the  $\Delta G_a^\circ$  at 423 K are to be preferred by far.

The electron attachment enthalpies  $\Delta H_a^\circ$ , given in Table I, originate from the  $\Delta H_a^\circ$  scale in Figure 3 for the compounds for which van't Hoff plots were obtained. For the remaining compounds the  $\Delta H_a^\circ$  were evaluated from eq 5, the  $\Delta G_a^\circ$  from Figure 1 and the estimated  $\Delta S_a^\circ$  given in Table I.

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (5)$$

The electron affinities given in Table I are the  $\Delta H_a^\circ$  values of Table I with inverted sign and converted to electron volt, i.e., the approximation,  $EA = -\Delta H_a^\circ$ , was made. It should be noted that the stationary electron convention<sup>9</sup> was used for the evaluation of  $\Delta G_a^\circ$  and  $\Delta S_a^\circ$ .

There are several determinations in the literature with which the present data can be compared. Experimental gas-phase determinations of the threshold for the endothermic charge transfer:  $Cs + B = Cs^+ + B^-$ , by Compton et al.,<sup>3</sup> led to  $EA = 1.4 \pm 0.2$  eV, for maleic anhydride, in good agreement with the present 1.44 eV result.

Fukuda and McIver<sup>10</sup> have determined relative electron attachment free energies, i.e., a scale of  $\Delta G_{et}^\circ$  which when calibrated to the present scale<sup>6</sup> lead to  $\Delta G_a^\circ$  values for  $\sim 380$  K. The values obtained for maleic and phthalic anhydride are essentially identical with the present results, see Table I.

The values of Chen and Wentworth<sup>11</sup> based on electron transfer charge spectra in solution  $E_{CT}$  and polarographic reduction potentials  $E_{1/2}$  are also in fair agreement. The largest deviation is observed for tetrachloro phthalic anhydride: 1.95 eV, present results, versus 1.7 eV from  $E_{CT}$  and 1.6 eV from  $E_{1/2}$ , see Table I. The lower  $E_{CT}$  and  $E_{1/2}$  values are probably due to the neglect of the change of coulombic and solvation interactions that occur for charge delocalized ions,<sup>6</sup> see section c this work.

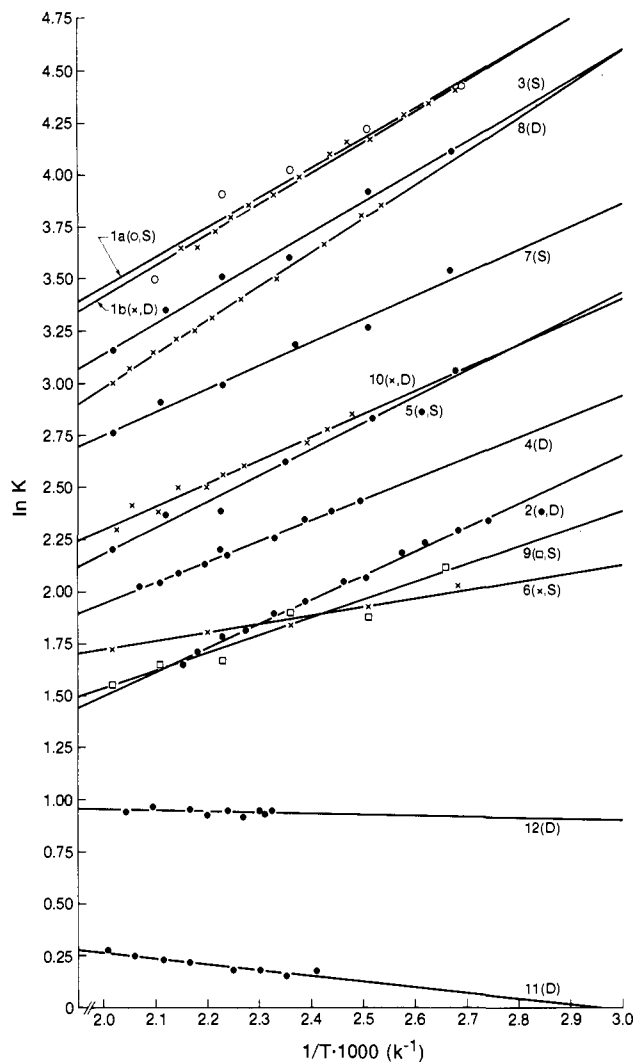
**b. Effect of Substituents on the Electron Affinities.** The electron affinities of the substituted maleic and phthalic anhydrides are compared with those of similarly substituted benzo- and naphthoquinones<sup>7</sup> (data in brackets) in Figure 5. The extra electron in both types of systems enters the LUMO, which is a  $\pi^*$  orbital resulting from a combination of  $\pi^*_{C-C}$  and two  $\pi^*_{C=O}$ . As expected, from the smaller extent of conjugation in the anhydrides, their LUMO energies are higher, which leads to lower EA for these compounds relative to the quinones. Thus, the EA of maleic anhydride is  $\sim 10$  kcal/mol lower than that for benzoquinone. Substitution by the electron-donating methyl destabilizes the LUMO's of the quinones<sup>7</sup> and the anhydrides. The effect is larger for the anhydrides whose  $\pi$  systems are somewhat more localized. Thus, two methyls decrease the EA of benzoquinone by only 3 kcal/mol, while the decrease is 6.4 kcal/mol for maleic anhydride, see Figure 5. Similarly the stabilizing effects of electron-withdrawing substituents like phenyl or chlorine are larger for the anhydrides. Thus Ph increases the EA of benzoquinone by 2.7 kcal/mol and that of maleic anhydride by 6 kcal/mol, see Figure 5. The change from benzoquinone to anthroquinone leads to a decrease of the electron affinity by 2.2 kcal/mol,<sup>7</sup> while the analogous change from maleic to phthalic anhydride leads to the larger decrease of 5.4 kcal/mol.

The more remote substitution by electron-withdrawing substituents on the benzene group of the phthalic anhydride also leads to significant increases of the electron affinity. Thus substitution

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(11) Chen, E. C. M.; Wentworth, W. E. *J. Chem. Phys.* **1975**, *63*, 3183.

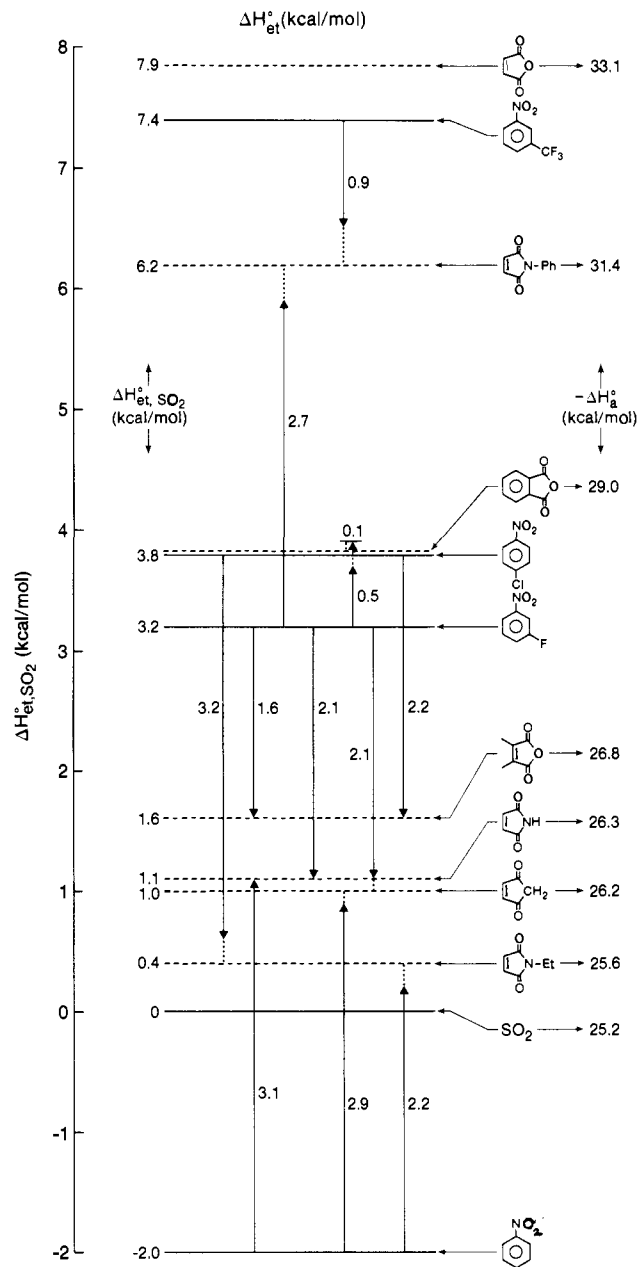


**Figure 2.** van't Hoff plots of electron-transfer equilibrium constants  $K_{et}$ . Numbers identify reactions given in Figure 3. In some of the individual measurements (S) static temperatures were used. In others, measurements were made as the temperature decreased slowly (D).

with two Cl atoms in positions 3,6 leads to an increase of 9.8 kcal/mol. This effect is almost as large as the Cl substituent effect in 1,2-dichloromaleic anhydride, which is 10.7 kcal/mol. One would have expected a considerably smaller increase for the more remote substitution in phthalic anhydride because the stabilization is largely due to  $\sigma$  withdrawal by Cl and the polarizability of Cl. The relatively large effect is probably due to the lesser destabilization due to  $\pi$  donation by the Cl atoms when they are on the benzene ring when compared to the 1,2 positions in maleic anhydride.

Nitro substitution in phthalic anhydride has a very large effect on the electron affinity which is increased by  $\sim 20$  kcal/mol. This can be compared to the  $\sim 22$  kcal/mol change from nitrobenzene EA (22.8 kcal/mol) to *p*-dinitrobenzene EA (44.3 kcal/mol).<sup>6</sup> The EA of the 4-NO<sub>2</sub> substituted phthalic anhydride is  $\sim 2$  kcal/mol higher than that for the 3-NO<sub>2</sub> isomer, see Figure 5. This is probably due to the larger coulombic repulsion between the negative charge on the adjacent CHO and NO<sub>2</sub> groups in the 3-NO<sub>2</sub> substituted phthalic anhydride radical anion. It may be noted that the nitro substituted phthalic anhydrides also can be considered as doubly CHO substituted nitrobenzenes. The 4-NO<sub>2</sub> substituted phthalic anhydride becomes the *m,p*-di-CHO substituted isomer which is expected<sup>6,12</sup> to have a higher EA than

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**Figure 3.** Scale of electron-transfer enthalpies  $\Delta H_{et}^0$  based on van't Hoff plots shown in Figure 2.  $\Delta H_{et}^0$  given in numbers beside arrows with decimal point. Number below identifies plot in Figure 2.  $-\Delta H_a^0$  for  $e + B = B^-$ , given in the right column.

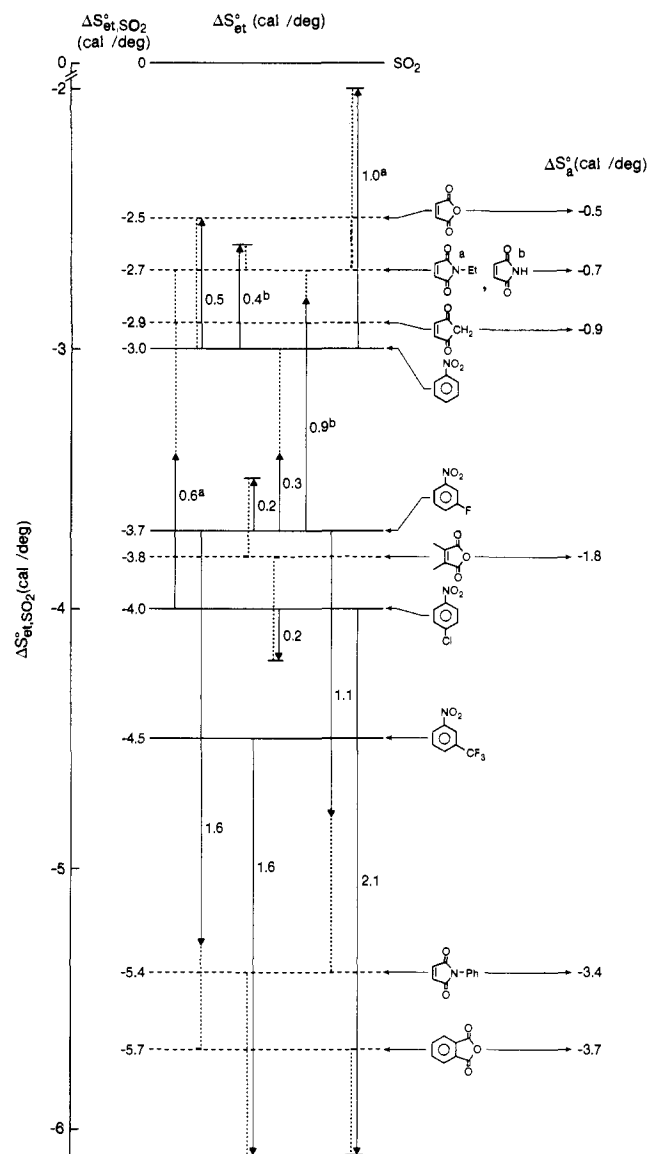
the *o,m*-di-CHO compound, i.e., the 3-NO<sub>2</sub> phthalic anhydride.

It is interesting to note that the electron affinity of the pyridine analogue of phthalic anhydride (EA = 30.7 kcal/mol) is somewhat larger than that of phthalic anhydride (EA = 27.4 kcal/mol), Figure 5. This probably reflects a lowering of the  $\pi^*$  LUMO by the higher electronegativity of the N atom relative to the C atom. Recent measurements,<sup>13</sup> which gave a higher EA for pentafluoropyridine relative to hexafluorobenzene should be due to the same effect. Electron transmission spectroscopy studies of the temporary negative ion states of benzene and pyridine by Burrow, Jordan et al.<sup>14</sup> have shown that EA(pyridine) is about 12 kcal/mol higher than EA(benzene). This difference can also be attributed<sup>15</sup>

(13) Dillow, G. W.; Kebarle, P. *J. Am. Chem. Soc.* **1988**, *110*, 4877-4882.

(14) Burrow, P. D.; Ashe, III, A. J.; Bellville, D. J.; Jordan, K. D. *J. Am. Chem. Soc.* **1982**, *104*, 425.

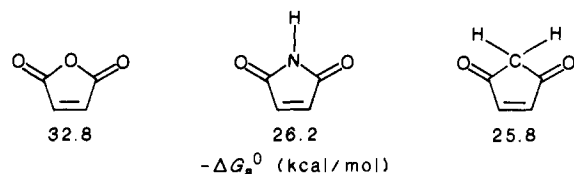
(15) The presence of more electronegative N causes a splitting of the degenerate  $e_{2u}$  LUMO of benzene into two orbitals, where the lower one  $b_1(\pi^*)$  becomes the LUMO in pyridine, for more detail see Burrow et al.<sup>14</sup>



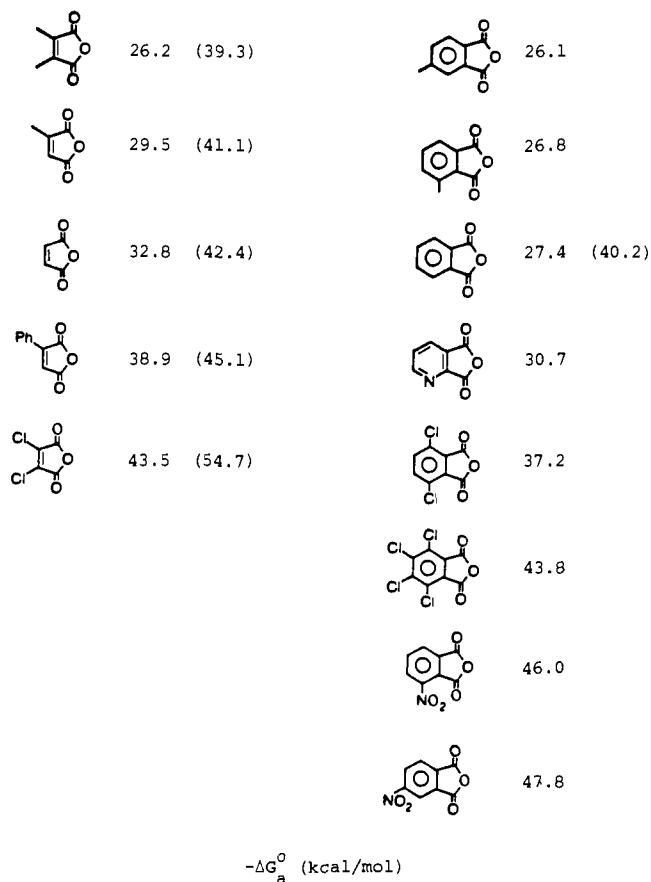
**Figure 4.** Entropy changes,  $\Delta S_{et}^{\circ}$ , for electron-transfer reactions from van't Hoff plots in Figure 2. Solid lines, actual measurements. Dotted lines connect actual measurements to compound involved.

to the higher electronegativity of N relative to C.

The electron attachment energies for the cyclic dicarbonyls with bridging O, NH, and  $\text{CH}_2$ , from Table I, are given below. The



electron affinity of the oxy compound is 6.5 kcal/mol larger than that of the NH and  $\text{CH}_2$  bridged structures. Methoxy substitution of benzoquinone was found to lead to a small decrease of the electron affinity. This was assumed to be due to the destabilizing effect of  $\pi$  donation by the oxygen. A similar destabilization can be expected also in maleic anhydride. This however is counteracted by  $\sigma$  withdrawal due to the large electronegativity of the oxygen so that a net stabilization of the  $\pi^*$  LUMO results. For nitrogen, in maleimide, the  $\pi$  destabilization should be similar and since the electronegativity is lower and further lowered by the presence of H, the  $\pi$  destabilization is barely overbalanced by  $\sigma$  withdrawal and the electron affinity ends up to be similar to that for the  $\text{CH}_2$  bridged cycloaddition where there is essentially no destabilization by  $\pi$  donation and no stabilization by  $\sigma$  withdrawal.



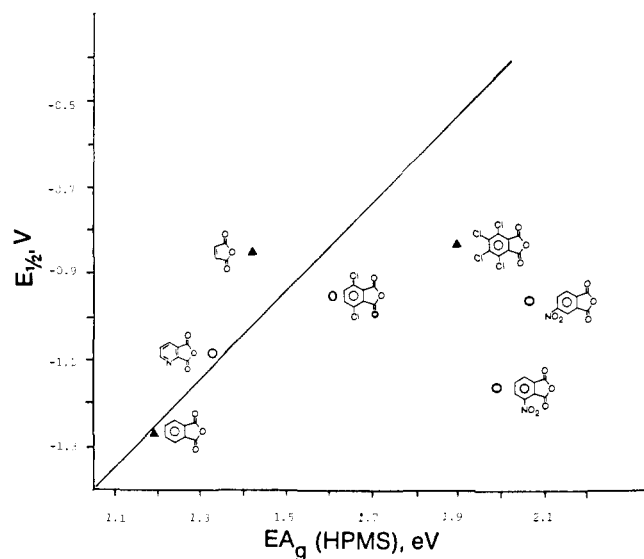
**Figure 5.** Electron attachment free energies  $-\Delta G_a^{\circ}$  for the maleic and phthalic anhydrides. Values given in brackets are the  $-\Delta G_a^{\circ}$  for the corresponding quinones.<sup>7</sup>

For maleimide the data in Table I provide some information for substitution on the N atom. Thus Me or Et substitution decrease the electron affinity by less than 1 kcal/mol, an effect much smaller than the 3 kcal/mol decrease for Me substitution on  $\text{sp}^2$  carbon in maleic anhydride. Similarly Ph substitution on N in maleimide increases the electron affinity by 3.8 kcal/mol, while in maleic anhydride the increase is by 6 kcal/mol. The smaller effects for maleimide are expected, since with regard to the  $\pi^*_{\text{CO}}$  and  $\pi^*_{\text{C=C}}$  system which determines the electron affinity, the substitution on N in maleimide is relatively remote.

Unfortunately, recent theoretical calculations concerning the LUMO's and the electron affinities of the cyclic dicarbonyls I and II have not been reported; however, results from earlier work are available. This work was stimulated by interest in correlations of the occupied orbital energies with the ionization potentials and unoccupied orbitals with electron affinities<sup>16-18</sup> within the context of Koopmans' theorem. Of primary interest are the HOMO and LUMO which are also of importance in lowest energy electronic spectra<sup>19,20</sup> and Frontier molecular orbital theory which relates chemical reactivity to these orbitals as, for example, for nucleophilic and cycloadditions to quinones<sup>21</sup> and to the anhydrides, I and II.

Kunii and Kuroda,<sup>16</sup> using the Pariser-Parr-Pople approximation to the Hartree-Fock equation with an adjusted core parameter  $\beta$ , obtained IP and EA for 30 heteroaromatic compounds

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**Figure 6.** Polarographic halfwave potentials in dimethylformamide (DMF) versus gas phase electron attachment free energies ( $-\Delta G_a^\circ$ ). Solid line corresponds to slope = 1 expected if assumption is made that the solvation energies in DMF are constant, see eq 6 in text. Lack of correlation for present compounds demonstrates importance of changing solvation energies: ( $\blacktriangle$ )  $E_{1/2}$  from Peover;<sup>22</sup> ( $\circ$ )  $E_{1/2}$  from Nagy.<sup>24</sup>

including the EA for maleic anhydride (1.43 eV) and phthalic anhydride (0.99 eV). These results are fairly close to the present values of 1.4 and 1.2 eV, see Table I. Later work by Compton et al.<sup>17</sup> with the same formalism but an adjustable  $\beta$  and  $\gamma$  provided IP and EA for some 100 heteroaromatic compounds including the EA for maleic anhydride (1.0 eV) and maleimide (0.94 eV) which are in fair agreement with the present results in Table I.

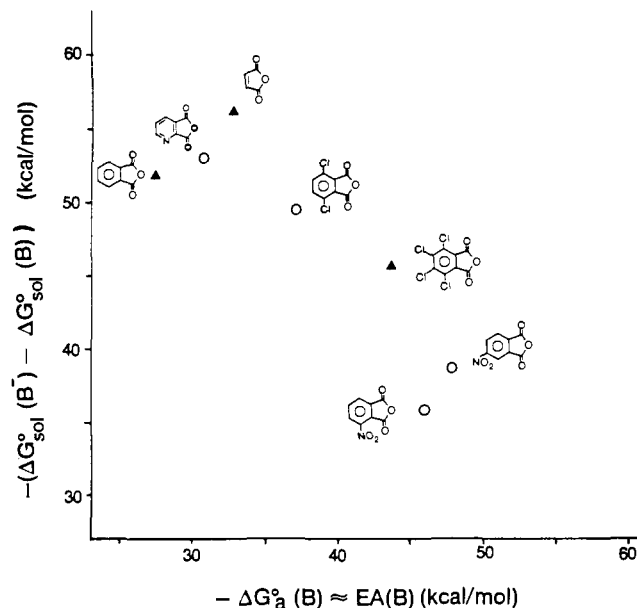
**c. Comparison with Reduction Potentials in Solution. Solvation Energy of the Radical Anions.** Several determinations of the polarographic halfwave reduction potential,  $E_{1/2}$ , relating to the reaction  $2, B + e = B^-$ , in solution, where  $B$  is the substituted cyclodienes I and II, have been reported.<sup>22-24</sup> On the basis of these data and the present determinations of the gas-phase reduction (electron attachment) energies one can examine how well the gas-phase data correlate with those in solution and also obtain approximate solvation energies for the radical anions  $B^-$ . Comparisons of this type for other systems were reported in previous work from this laboratory.<sup>6,7,25</sup> The eq 6 used<sup>7</sup> is based on a Born type cycle for the reduction reaction 2 in the gas phase and solution.<sup>7,26</sup> The  $\Delta G_a^\circ(B)$  is the electron attachment free energy  $EA(B) \approx -\Delta G_a^\circ(B) =$

$$+23.06E_{1/2}(B) + (\Delta G_{sol}^\circ(B^-) - \Delta G_{sol}^\circ(B)) + 108.6 \quad (6)$$



( $-\Delta G_a^\circ(B) \approx EA(B)$ ), see Table I, in kcal/mol,  $E_{1/2}(B)$  is the polarographic reduction potential in volt versus the calomel electrode, and the solvation energies  $\Delta G^\circ(B)_{sol}$ ,  $\Delta G^\circ(B^-)_{sol}$  are defined in (7). The numerical constant 108.6 (kcal/mol) leads to these quantities being in kcal/mol units.

A plot of  $E_{1/2}(B)$ , obtained by Peover<sup>22</sup> and Nagy<sup>24</sup> in dimethylformamide, DMF, versus the SCE, is shown in Figure 6 plotted versus  $EA \approx -\Delta G_a^\circ$ . It is evident that for this group of compounds the correlation between  $E_{1/2}$  and EA is poor.  $E_{1/2}$



**Figure 7.** Solvation energies  $\Delta\Delta G_{sol}^\circ = \Delta G_{sol}^\circ(B^-) - \Delta G_{sol}^\circ(B)$  deduced with eq 6 from  $E_{1/2}$  shown in Figure 6 and present  $\Delta G_a^\circ$  results.  $\Delta\Delta G_{sol}^\circ$  is dominated by  $\Delta G_{sol}^\circ(B^-)$ , see text. Large decreases of solvation exothermicity for  $B^-$  with increasing electron affinity ( $-\Delta G_a^\circ(B)$ ) are due to increasing charge delocalization in  $B^-$ .

data from different laboratories are taken under somewhat different conditions and may be displaced by a constant value. Therefore, it is significant in Figure 5 that the  $E_{1/2}$  data originating from the same laboratory show no significantly better correlation with the EA values. Furthermore, it is the high EA compounds that have EA values that are relatively much higher than the corresponding  $E_{1/2}$  data, i.e., these compounds are found far to the right of the unit slope line in Figure 5. This suggests that the trends observed are real and that significant changes in  $\Delta G_{sol}^\circ(B^-) - \Delta G_{sol}^\circ(B)$  occur within this series of compounds.

The solvation energy difference  $\Delta\Delta G_{sol}^\circ = \Delta G_{sol}^\circ(B^-) - \Delta G_{sol}^\circ(B)$ , evaluated with eq 6 from the data in Figure 5, is shown in Figure 6. These results show that the solvation exothermicity,  $-\Delta\Delta G_{sol}^\circ$ , is smallest for the highest EA compounds. Significantly these are the compounds substituted with the strongest electron-withdrawing groups:  $NO_2$  or multiply substituted by Cl, i.e., the radical anions with the largest charge delocalization for which the lowest  $-\Delta G^\circ(B^-)_{sol}$  are expected since it is known that charge delocalization leads to a decrease of solvation. It should be noted that the solvation exothermicity of  $B^-$  is very much larger than that of  $B$  and therefore  $\Delta\Delta G_{sol}^\circ$  is dominated by the  $\Delta G_{sol}^\circ(B^-)$  term. For example,  $\Delta G_{sol}^\circ(B^-)$ 's at 298°K for maleic and phthalic anhydride are approximately -6.5 and -7.8 kcal/mol,<sup>27,28</sup> which is close to 1/10 of the value for  $\Delta G_{sol}^\circ(B^-)$ , see Figure 6.

Similar  $\Delta G_{sol}^\circ(B^-)$  trends were found in earlier comparisons of EA with  $E_{1/2}$  values.<sup>6,7,25</sup> However for the present series of compounds the effects are very large. The scatter and deviation from unit slope in Figure 5 is very pronounced and correspondingly the differences in  $\Delta\Delta G_{sol}^\circ$  in Figure 6 are amongst the largest. A large difference was observed in earlier work<sup>25</sup> for  $NO_2$  substitutions:  $-\Delta\Delta G_{sol}^\circ$  (nitrobenzene)  $\approx$  58 kcal/mol and  $-\Delta\Delta G_{sol}^\circ$  (1,4-dinitrobenzene)  $\approx$  48 kcal/mol in DMF. These values and the difference are similar to the data in Figure 6 for phthalic anhydride and the nitrophthalic anhydrides, although the change in the latter group is  $\sim$  5 kcal/mol larger. This larger difference may be due to a true effect or experimental discrepancies caused by the different origin of the  $E_{1/2}$  data.

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(27) A rough estimate of  $\Delta G_{sol}^\circ(B)$  can be obtained from the equation:  $\Delta G_{sol}^\circ(B) \approx RT \ln(P_B/C_B)$ . The vapor pressures  $P_B$  over the pure liquid or solid were obtained from Stull et al.<sup>28</sup> (MaAn =  $3.7 \times 10^{-4}$  atm); (PhAn =  $5 \times 10^{-6}$  atm). The solubilities  $C_B$  in DMF were measured in this laboratory: (MaAn 22.8 mol/L), (PhAn 2.8 mol/L).

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Prior to the availability of the abundant gas-phase electron-transfer equilibria data,<sup>6</sup> electron affinities were often obtained<sup>1,2,11</sup> from available  $E_{1/2}$  values via eq 6 and the assumption that  $\Delta\Delta G_{\text{sol}}^{\circ}$  is constant, particularly in dipolar aprotic solvents like DMF. The results in Figures 5 and 6 show that for some groups of compounds this assumption breaks down and can lead to relative errors of 10 kcal/mol or more. Now that EA data are available, it is appropriate to concentrate on the solvation energies of the ions and their relative magnitudes and build up an extensive data

bank. The availability of abundant data will lead to a much needed improved understanding of ion solvation of diverse systems. Very desirable in this quest are extensive modern determinations of reduction potentials and their temperature dependence under standardized conditions. Fortunately some such work is being done.<sup>29</sup>

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## A Theoretical Study of the Potential Energy Surface of Butadiene in the Excited States

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**Abstract:** The molecular structures and the potential energy surfaces of the low-lying states of 1,3-butadiene are examined by using the ab initio MCSCF method. The equilibrium structures of *cis*-butadiene in the excited states are very similar to those of *trans*-butadiene. While single  $\pi \rightarrow \pi^*$  excitation leads to the twisting of one C-C double bond, the doubly excited  $\pi \rightarrow \pi^*$  state has a very flat potential energy surface for the torsion of all C-C bonds. The contribution of this  $\pi \rightarrow \pi^*$  excited state to *cis*-*trans* isomerization and ring closure reactions is discussed.

### I. Introduction

The study of the excited states of olefins is a subject of great importance in understanding spectroscopic data as well as mechanisms of photochemical reactions.<sup>1</sup> The electronically excited states of molecules which contain  $\pi$  electrons play an important role in the reactions induced by photons, such as photoisomerization, photodecomposition, or cycloaddition reactions.<sup>2</sup> Although the Woodward-Hoffmann rule<sup>3</sup> gives a beautiful explanation for the stereoselectivity of electrocyclic reactions, there is not enough evidence to support this rule in the case of reactions in the excited state. One of the reasons that few of the experimental results support this rule is that the chemistry occurring in the excited states is very complicated and often varies depending on the reaction conditions. Another important reason is that several excited states are generated upon irradiation.

The excited states of  $\pi$ -electron systems are especially complex in that the different states have different electronic character. Such differences may be influenced by the strong effect of substituents, which may lead to reaction along different potential surfaces. This feature can be even seen in ethylene which has only one double bond. Ethylene has a twisted equilibrium structure in the lowest triplet and two low-lying excited singlet states, and the energies of these states are very close to each other.<sup>4</sup> It is known that the lowest excited singlet state has ionic character and the triplet and ground states have biradical nature at the twisted geometry. Given these considerations, the cycloaddition of two ethylene molecules in the excited state does not seem to be a concerted reaction. It is obvious that the Woodward-Hoffmann rule does not apply to the case of a reaction via biradical or excited states.

There are more low-lying excited states when the ethylenic units are conjugated. In a previous paper,<sup>5</sup> we have studied the potential energy surfaces of *trans*-butadiene in the low-lying states. While the ground state of butadiene maintains the planarity due to  $\pi$  electron delocalization, the molecular structures in the excited

states are no longer planar. The previous calculation<sup>5</sup> shows that the equilibrium structures are very different in each electronic state. It is even more interesting that there exists a doubly excited singlet state which arises from the coupling of two triplet states of each ethylene unit.<sup>6</sup>

Another interesting aspect lies in the possibility of butadiene undergoing an electrocyclic reaction.<sup>3</sup> Although *trans*-butadiene is thermally stable, less stable *cis*-butadiene can undergo electrocyclization to cyclobutene. In this respect, a *cis*-*trans* isomerization process should also be considered in the course of thermal or photochemical reactions. It is known that the barrier height from *trans*-butadiene to *cis*-butadiene is 5 kcal/mol in the ground state.<sup>7</sup> In the excited states, however, isomerization can occur at two different positions, namely, the terminal C-C bond or center C-C bond.

In order to explore the electronic states which play an important role in the photochemical reactions of species containing two double bonds, we have conducted a theoretical study of the potential energy surfaces of the low-lying states of *cis*-butadiene as well as the *trans* form. One might expect to find a relationship between geometrical relaxation in the excited states of *cis*-butadiene and isomerization or ring closure reaction paths, even though *cis*-butadiene is less stable in the ground state. We will elaborate on these considerations in conjunction with our results in the last part of this paper.

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