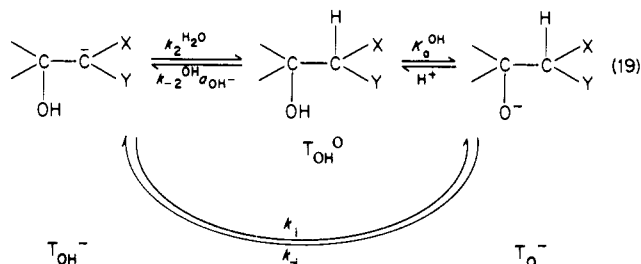


the same base. This indicates that the competing k_i - k_{-i} pathway (eq 19), which involves an intramolecular proton switch,²³ plays a minor, if any, role in the BID system.



This is consistent with the behavior of **1** and **2**. However, it contrasts with our findings for **3**^{2,5b} where the k_i - k_{-i} pathway contributes significantly to the reaction; i.e., $k_2^{H_2O}$ has to be replaced by $k_2^{H_2O} + k_i$ and k_{-2}^{OH} by $k_{-2}^{OH} + K_a^{OH}k_{-i}/K_w$, with k_i and $K_a^{OH}k_{-i}/K_w$ being actually the dominant terms. The reasons why the intramolecular proton switch is a significant pathway in some systems but not in others have been discussed elsewhere.²⁴

Experimental Section

Materials. 1,3-Indandione (Aldrich) was recrystallized from 100% ethanol, mp 130–131 °C (lit. 130 °C²⁵) prior to use. Benzylidene-1,3-indandione (BID) was prepared from benzaldehyde and 1,3-indandione in ethanol, with piperidine as catalyst, according to the procedure of Behera and Nayak,²⁶ mp 152 °C (lit. 152–153 °C²⁷). Benzaldehyde was

(23) Such an intramolecular proton switch most likely involves a water bridge in the transition state.²⁴

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purified by washing, drying, and vacuum distillation, according to the method of Perrin.²⁸

Phenols were recrystallized from hexane prior to use. Chloroacetic acid was recrystallized from petroleum ether. Methoxyacetic acid was distilled, and piperidine was distilled following refluxing over CaH₂. All other reagents were commercial products used without further purification.

Kinetics. The fast reactions were monitored on a Durrum stopped-flow apparatus with computerized data handling.²⁹ For OH⁻ and PhO⁻ addition, KOH or buffered PhOH solutions were mixed with solutions of BID containing a little HCl (to prevent hydrolysis in the reservoir syringe).

The slow reactions were measured in a Perkin-Elmer Model 559A spectrophotometer. In most cases, cuvettes containing buffer solution were equilibrated at 20 °C, and either BID or ID, followed (after a few minutes) by benzaldehyde, was added by injecting a few microliters of concentrated stock solution. For the slow conversion of TOH⁻ to products the usual method was the same as above, but a higher concentration of BID (5×10^{-4} M) was required in order to achieve high enough OD changes.

pH's were measured as described previously.⁵

Acknowledgment. This research was supported by Grant CHE-8315374 from the National Science Foundation.

Registry No. BID, 5381-33-9; ID, 606-23-5; PhCHO, 100-52-7.

Supplementary Material Available: Kinetic data, Tables S1–S10 (9 pages). Ordering information is given on any current masthead page.

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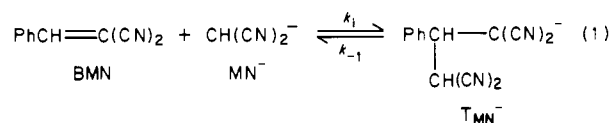
Nucleophilic Addition to Olefins.¹ 14. Kinetics of the Reaction of 1,3-Indandione Anion with Benzylidene-1,3-indandione

Claude F. Bernasconi,* Alan Laibelman, and Janie L. Zitomer

Contribution from the Thimann Laboratories of the University of California, Santa Cruz, California 95064. Received May 2, 1985

Abstract: The rate and equilibrium constants of the reversible addition of 1,3-indandione anion (ID⁻) to benzylidene-1,3-indandione (BID) have been determined in 50% Me₂SO–50% water at 20 °C: $k_1 = 7.23 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$, $k_{-1} = 9.35 \times 10^{-3} \text{ s}^{-1}$, $K_1 = 7.73 \times 10^5 \text{ M}^{-1}$. The *intrinsic* rate constant for this reaction is about 300-fold lower than for the analogous reaction of malononitrile anion (MN⁻) with benzylidenemalononitrile (BMN). This is consistent with numerous previous observations according to which reactions involving more strongly resonance-stabilized carbanions have lower intrinsic rates (higher intrinsic barriers). The ratio of 300 in the intrinsic rate constants is larger than the corresponding ratios in the addition of hydroxide ion to BMN vs. BID, or the addition of MN⁻ vs. ID⁻ to benzaldehyde. This is not surprising since the reactions of ID⁻ with BID and the one of MN⁻ with BMN both involve *two* carbanionic sites. Our results, as well as similar findings in the comparison of the MN⁻/BMN system with the nitromethane anion/ β -nitrostyrene system, constitute Marcus-type behavior, although the *quantitative* adherence to a modified Marcus equation is not very good. The pK_a values of both the keto and the enol form of the BID/ID⁻ adduct and proton-transfer rates involving the keto form were determined. The enol content of the adduct is much higher than that of ID itself. This is attributed to intramolecular hydrogen bonding in the adduct. Proton transfer at carbon of the adduct is, for a given ΔpK , slower by a factor of ~ 12 than at carbon of ID, showing the operation of a steric effect.

We recently reported a kinetic study of the Michael addition of malononitrile anion (MN⁻) to benzylidenemalononitrile (BMN) in water and in 50% Me₂SO–50% water.² In this latter solvent, the reaction has an equilibrium constant, $K_1 = k_1/k_{-1}$, of 1.45



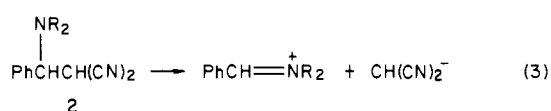
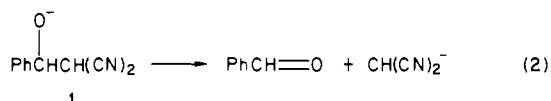
$\times 10^5 \text{ M}^{-1}$ and is quite rapid, with $k_1 = 9.50 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ and $k_{-1} = 6.52 \text{ s}^{-1}$.

The high rate constants are not surprising in the context of other reactions which lead to the formation or destruction of malono-

(1) Part 13: Bernasconi, C. F.; Laibelman, A.; Zitomer, J. L. *J. Am. Chem. Soc.*, preceding paper in this issue.

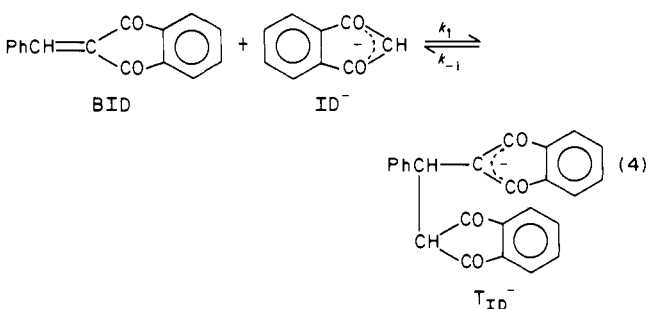
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nitrile-type anions. For example, protonation of malonitrile anions,³ addition of nucleophiles other than $\text{CH}(\text{CN})_2^-$ to BMN ,^{4,5} and the loss of $\text{CH}(\text{CN})_2^-$ from adducts such as **1**⁵ and **2**^{4,6} are



all quite fast when compared to analogous reactions involving other types of carbanions.⁷ In other words, the *intrinsic* rate constant, k_0 ⁸ (intrinsic barrier, ΔG^\ddagger_0), of reactions involving malonitrile-type anions is generally substantially higher (the intrinsic barrier is substantially lower) than for reactions involving other types of stabilized carbanions. This has been attributed to the smaller degree of resonance stabilization of malonitrile-type anions as compared with other carbanions such as nitronate ions, enolate ions, etc.⁷

We now wish to report a kinetic study of the Michael addition of 1,3-indandione anion (ID^-) to benzyldiene-1,3-indandione (BID).



reactions 1 and 4 would be of comparable magnitude because the lower basicity of ID^- compared with that of MN^- ($\text{p}K_{\text{a}}^{\text{ID}} = 6.35$,^{9,10} $\text{p}K_{\text{a}}^{\text{MN}} = 10.21$ ^{2,9}) should be compensated for by a higher stability of T_{ID}^- compared with that of T_{MN}^- . Thus a comparison of the rate constants for the two reactions should afford an approximate measure of the relative *intrinsic* rate constants, $k_0^{\text{ID}}/k_0^{\text{MN}}$ (or difference in the intrinsic barriers, $\Delta\Delta G^\ddagger_0$).

What makes a comparison of reactions 1 and 4 particularly interesting is that both involve *two* carbanionic sites. In reaction 1 there is concurrent formation and destruction of a "fast" carbanion while in eq 4 there is concurrent formation and destruction of a relatively "slow" carbanion. One therefore wonders whether the difference in intrinsic rates or intrinsic barriers will be magnified compared with reactions where only *one* carbanion is either formed or destroyed. Such enhancement of the difference in intrinsic rates would correspond to Marcus-type¹¹ behavior.

Our results will show that there is indeed such an enhancement but that it falls short of what one might expect on the basis of a quantitative application of a Marcus-type formalism. This study

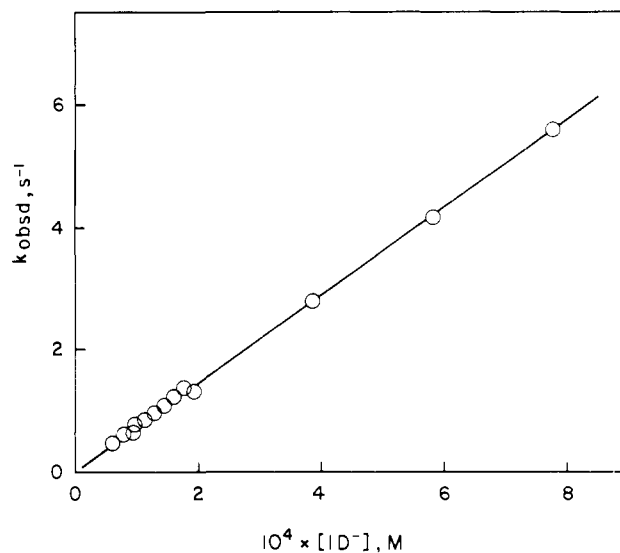


Figure 1. Kinetics of adduct formation between ID^- and BID.

also allowed a determination of the carbon and oxygen (enol) $\text{p}K_{\text{a}}$ of T_{ID}^- , and of the proton-transfer rates at carbon of T_{ID}^- .

Results

General Features. All experiments were conducted in 50% Me_2SO –50% water (v/v) at 20 °C. ID and BID are virtually insoluble in pure water; 50% Me_2SO was the solvent of choice because many of our previous studies were performed in this solvent.

Kinetic experiments were conducted under pseudo-first-order conditions with ID^- as the excess component. Constant pH was maintained by appropriate buffers. The ionic strength was kept at 0.5 M with KCl.

Formation of the Michael adduct T_{ID}^- was established by its UV/vis spectrum (λ_{max} 425 nm, ϵ 2250) which is quite similar to that of ID^- (λ_{max} 415 nm, ϵ 2300) and to that of the hydroxide ion adduct of BID (λ_{max} 430 nm, ϵ 2200).¹ BID has λ_{max} 343 nm, ϵ 19 500.

Kinetics of Adduct Formation. Rates were measured in the stopped-flow apparatus in dilute 4-cyanophenol buffers around pH 7.8 to 7.9. In this pH range ID is almost completely ionized ($\text{p}K_{\text{a}}^{\text{ID}} = 6.35$) and the hydrolysis of BID is negligibly slow.¹ Pseudo-first-order rate constants, k_{obsd} , were measured as a function of $[\text{ID}^-]$ by monitoring the disappearance of BID at 343 nm.

The results are summarized in Table S1 (supplementary materials).¹² A plot of k_{obsd} vs. $[\text{ID}^-]$ is shown in Figure 1. It affords $k_1 = 7.23 \pm 0.02 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$. The intercept (k_{-1}) is indistinguishable from zero.

pH-Jump Experiments. In order to evaluate k_{-1} the equilibrium was approached from the adduct side. T_{ID}^- was generated in a pH 8–9 solution. This solution was then subjected to a pH jump by mixing it with an acidic carboxylate buffer or an HCl solution, either in the stopped-flow apparatus or in a conventional spectrophotometer.

When the reaction was monitored at 425 nm (λ_{max} of T_{ID}^-) a relatively rapid (30–300 ms) loss of OD was observed. Monitoring the reaction at 343 nm (λ_{max} of BID) showed an increase in OD, but this increase was much slower (10^2 – 10^4 s) than the disappearance of T_{ID}^- at 425 nm.

The results obtained in HCl solution are summarized in Table I; τ_1^{-1} designates the pseudo-first-order rate constant for the first, τ_2^{-1} for the second process. Figure 2 shows that τ_1^{-1} increases with increasing hydrogen ion activity up to a point and then levels off. On the other hand, τ_2^{-1} decreases with decreasing pH; the latter data are plotted as $(\tau_2^{-1})^{-1} = \tau_2$ vs. a_{H^+} in Figure 3. Additional data, summarized in Table S2¹² (32 τ_1^{-1} values and 23

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(8) k_0 is defined as the rate constant when the equilibrium constant is unity; ΔG^\ddagger_0 is defined as ΔG^\ddagger when $\Delta G^\circ = 0$.

(9) In 50% Me_2SO –50% water at 20 °C.

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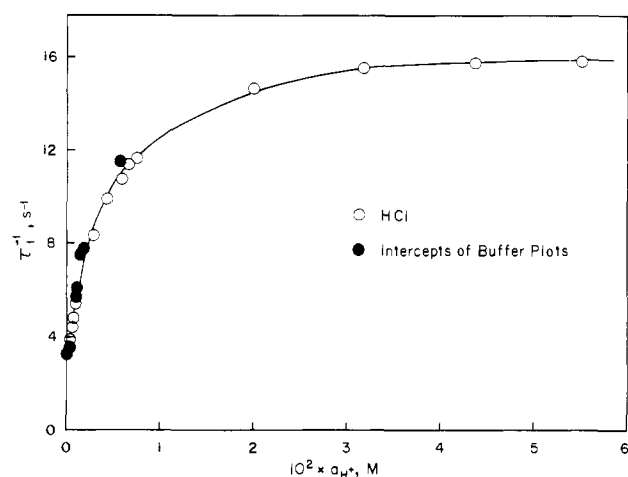
(11) (a) Marcus, R. A. *J. Phys. Chem.* **1968**, *72*, 891. (b) Cohen, A. O.; Marcus, R. A. *Ibid.* **1968**, *72*, 4249. (c) Albery, W. J. *Annu. Rev. Phys. Chem.* **1980**, *31*, 227.

Table I. pH-Jump Experiments in HCl Solution in 50% Me₂SO–50% Water at 20 °C

pH	$\tau_1^{-1},^b$ s ⁻¹	$10^4 \times \tau_2^{-1},^c$ s ⁻¹
1.24		0.737
1.26	15.8	
1.34		0.884
1.36	15.7	
1.48		1.16
1.50	15.5	
1.67		1.89
1.70	14.6	4.65
2.10		
2.13	11.6	7.82
2.18	11.3	
2.23	10.7	8.29
2.37	9.85	10.8
2.54	8.36	
3.03	5.73	28.9
3.09	5.35	33.5
3.18	4.76	36.3
3.28	4.38	42.2
3.43	3.87	

^a $\mu = 0.5$ M (KCl), $[T_{ID}^-]_0 \approx 10^{-4}$ M (see Experimental Section).

^b Loss of T_{ID}^- at 425 nm. ^c Formation of BID at 343 nm.

**Figure 2.** Dependence of τ_1^{-1} on a_{H^+} according to eq 6; from pH-jump experiments.

τ_2^{-1} values), indicate strong, linear buffer dependence of τ_1^{-1} , but no buffer dependence for τ_2^{-1} .

We offer the following interpretation. The τ_1^{-1} process refers to carbon protonation of T_{ID}^- , with rapid oxygen protonation (enol formation) acting as a rapid preequilibrium, as shown in Scheme I. According to this scheme, τ_1^{-1} is given by

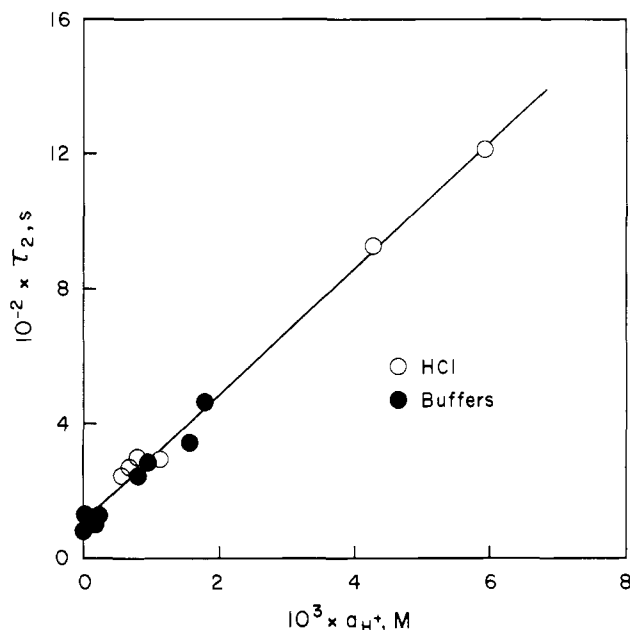
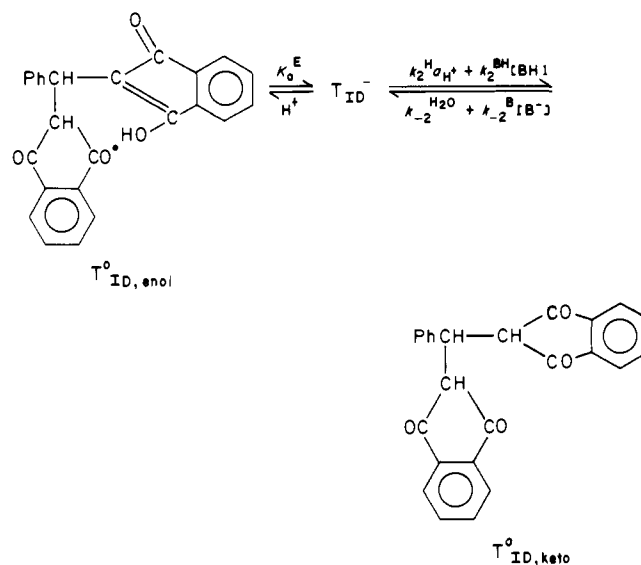
$$\tau_1^{-1} = \frac{K_a^E}{K_a^E + a_{H^+}} (k_2^H a_{H^+} + k_2^{BH} [BH]) + k_{-2}^{H_2O} + k_{-2}^B [B^-] \quad (5)$$

or, in the absence of buffer, by

$$\tau_1^{-1} = \frac{K_a^E}{K_a^E + a_{H^+}} k_2^H a_{H^+} + k_{-2}^{H_2O} \quad (6)$$

The curvilinear plot of Figure 2 is consistent with eq 6; the best fit is obtained with $k_2^H = 3.17 \pm 0.08 \times 10^3$ M⁻¹ s⁻¹, $k_{-2}^{H_2O} = 2.82 \pm 0.13$ s⁻¹, and $K_a^E = 4.33 \pm 0.30 \times 10^{-4}$ M ($pK_a^E = 2.36 \pm 0.03$). The acid dissociation constant of T_{ID}^0 (keto form) is then found as $K_a^K = k_{-2}^{H_2O}/k_2^H = 8.90 \pm 0.70 \times 10^{-4}$ M ($pK_a^K = 3.05 \pm 0.04$).

(12) See paragraph concerning supplementary material at the end of this paper.

**Figure 3.** Dependence of τ_2 on a_{H^+} according to eq 10; from pH-jump experiments.**Scheme I****Table II.** Rate Constants for Proton Transfer at Carbon of the ID Adduct of BID in 50% Me₂SO–50% Water at 20 °C

BH	pK_a^{BH}	$k_2^{BH},$ M ⁻¹ s ⁻¹	$k_{-2}^B,$ M ⁻¹ s ⁻¹
H ₃ O ⁺	-1.44	3.17×10^3	2.82/27.6
Cl ₂ CHCOOH	2.15	2.91×10^2	36.6
ClCH ₂ COOH	3.71	70.4	3.21×10^2
MeOCH ₂ COOH	4.54	28.0	9.05×10^2

^a $\mu = 0.5$ M (KCl).

The slopes of the plots of τ_1^{-1} vs. buffer acid concentration (not shown) are given by

$$\text{slope} = \frac{K_a^E}{K_a^E + a_{H^+}} k_2^{BH} + \frac{K_a^{BH}}{a_{H^+}} k_{-2}^B \quad (7)$$

with K_a^{BH} being the acid dissociation constant of the buffer. Equation 7 is equivalent to

$$\text{slope} = k_2^{BH} \left(\frac{K_a^E}{K_a^E + a_{H^+}} + \frac{K_a^K}{a_{H^+}} \right) \quad (8)$$

Scheme II

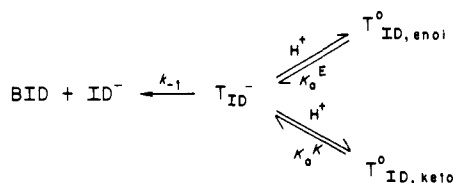


Table III. Rate and Equilibrium Constants for the Reaction of ID⁻ with BID (Eq 4) and Miscellaneous pK_a Values^a

constant	value
$k_1, \text{M}^{-1} \text{s}^{-1}$	$7.23 \pm 0.20 \times 10^3$
k_{-1}, s^{-1}	$9.35 \pm 1.50 \times 10^{-3}$
$K_1 = k_1/k_{-1}, \text{M}^{-1}$	$7.73 \pm 1.40 \times 10^5$
$\text{p}K_a^K$	3.05 ± 0.04
$\text{p}K_a^E$	2.36 ± 0.03
$K_E(\text{T-ID}^0)^b$	0.204
$\text{p}K_a^{\text{ID}}(\text{keto})^c$	6.35
$\text{p}K_a^{\text{ID}}(\text{enol})^c$	3.52
$K_E(\text{ID})^{b,c}$	1.48×10^{-3}

^aIn 50% Me₂SO-50% water at 20 °C, $\mu = 0.5 \text{ M}$ (KCl).

^bEnolization constant, $K_E = K_a^K/K_a^E$ or $K_a^{\text{ID}}(\text{keto})/K_a^{\text{ID}}(\text{enol})$, respectively, with K_a^K and K_a^E referring to the adduct T-ID⁰, K_a^{ID} to ID.

^cReference 10.

k_2^{BH} and k_{-2}^{B} values thus obtained for methoxy-, chloro-, and dichloroacetic acid are summarized in Table II.

The τ_2^{-1} process is associated with the recovery of BID, with both oxygen and carbon protonation of T-ID⁻ acting as fast pre-equilibria. This is shown in Scheme II. τ_2^{-1} is given by

$$\tau_2^{-1} = k_{-1} \frac{1}{1 + a_{\text{H}^+}(1/K_a^E + 1/K_a^K)} \quad (9)$$

or, after inversion

$$\tau_2 = \frac{1}{k_{-1}} + \frac{a_{\text{H}^+}}{k_{-1}}(1/K_a^E + 1/K_a^K) \quad (10)$$

From the plot according to eq 10 (Figure 3) one obtains $k_{-1} = 9.35 \pm 1.5 \times 10^{-3} \text{ s}^{-1}$ and $1/K_a^E + 1/K_a^K = 1.76 \pm 0.25 \times 10^3 \text{ M}^{-1}$. This latter value is in good agreement with $1/K_a^E + 1/K_a^K = 1.35 \times 10^3 \text{ M}^{-1}$ calculated from $\text{p}K_a^E$ and $\text{p}K_a^K$ evaluated from τ_1^{-1} .

Discussion

The rate and equilibrium constants determined in this study are summarized in Table II (proton transfer between T-ID⁻ and T-ID⁰_{keto}, Scheme I) and Table III (eq 4 and miscellaneous equilibrium constants). Table IV compares relevant parameters of the BID/ID⁻ system (eq 4) with those of the BMN/MN⁻ system (eq 1).

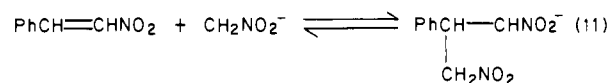
The BID/ID⁻ vs. the BMN/MN⁻ System. A. Equilibrium Constants. Considering the large difference in $\text{p}K_a$ between ID (6.35) and MN (10.21), the equilibrium constants, K_1 (Table IV), for carbanion addition are remarkably similar for the two systems ($7.73 \times 10^5 \text{ M}^{-1}$ for BID/ID⁻, $1.45 \times 10^5 \text{ M}^{-1}$ for BMN/MN⁻). As stated in the Introduction this is not unexpected; the lower basicity of ID⁻ which reflects its greater stability compared to that of MN⁻ is compensated for by the greater stability of the ID⁻-type anion in the adduct. Nevertheless, the equilibrium constants are not identical, K_1 for the BID/ID⁻ system being about fivefold larger than that for the BMN/MN⁻ system.

No firm conclusions can be drawn from this small difference in K_1 because of a paucity of systematic data on such equilibrium constants and a lack of a thorough understanding of all the factors which affect equilibrium constants in the addition of bases to activated olefins.¹

B. Intrinsic Rates. The rate constants k_1 and k_{-1} for the BID/ID⁻ system are both substantially lower than those for the BMN/MN⁻ system (ratios in last column of Table IV), indicating a lower intrinsic rate constant (higher intrinsic barrier) for the

BID/ID⁻ system, as anticipated. In order to correct for the slight difference in the equilibrium constants between the two systems, we adjust k_1 and k_{-1} for the BID/ID⁻ system in such a way as to make K_1 identical with the equilibrium constant for the BMN/MN⁻ system. This requires a slight reduction in k_1 and a slight increase in k_{-1} . We assume that the "Bronsted slope", $d \log k_1/d \log K_1 = -d \log k_{-1}/d \log K_1 = 0.5$ for this adjustment, and the adjusted k_1 and k_{-1} values are given in parentheses in Table IV.

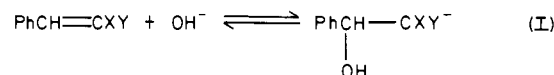
The ratio $k_1^{\text{MN}}/k_1^{\text{ID}} = k_{-1}^{\text{MN}}/k_{-1}^{\text{ID}} = 304$ (using the adjusted k_1^{ID} and k_{-1}^{ID} values) can be regarded as an approximation of the ratio of the intrinsic rate constants, $k_0^{\text{MN}}/k_0^{\text{ID}}$ ($\log(k_0^{\text{MN}}/k_0^{\text{ID}}) \approx 2.48$). In a similar way we have recently estimated $\log(k_0^{\text{MN}}/k_0^{\text{NO}_2}) \approx 5.7$ with $k_0^{\text{NO}_2}$ being the intrinsic rate constant for the reaction¹³



In view of the numerous recent endeavors at correlating intrinsic barriers of a variety of chemical reactions with the Marcus equation,^{11,14-17} it seems worthwhile to ask whether our results could be fit into a Marcus formalism. The notion that intrinsic barriers of "cross reactions" can be expressed as the arithmetic mean of the intrinsic barriers of the corresponding "identity reactions" in electron,¹¹ proton,¹¹ and methyl transfer reactions^{11,14} is one of the most interesting aspects of the Marcus treatment. However, its application to reactions for which no identity reactions can be defined^{11c,15-17} is more questionable, and for simple additions of nucleophiles to cations Ritchie¹⁸ has strongly argued against such application.

With nucleophilic additions to activated olefins and to carbonyl carbon the situation seems less clear-cut. This is because these reactions bear some resemblance to substitution reactions in the sense that there is a "leaving group" of sorts except that it does not leave,^{11c} and one can define "pseudo-identity" and "pseudo-cross" reactions as shown below. One may therefore arrive at a Marcus-type relation between the intrinsic barriers of pseudo-cross reactions and pseudo-identity reactions using the following reasoning.

Let us express the intrinsic barrier of reaction I

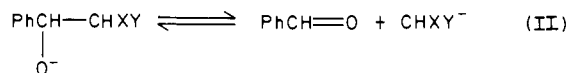


as

$$\Delta G_0^*(\text{eq I}) = \Delta G_0^*(\text{XY})_{\text{C=C}} + \Delta G_0^*(\text{O})_{\text{OH}^-} \quad (12)$$

$\Delta G_0^*(\text{XY})_{\text{C=C}}$ can be thought of as the contribution which comes from the conversion of the =CXY moiety to the -CXY⁻ moiety, while $\Delta G_0^*(\text{O})_{\text{OH}^-}$ is the contribution from the C-O bond formation between benzyl carbon and OH⁻.

In a similar way we can regard the intrinsic barrier of reaction II



as the sum of a contribution from the conversion of the -CHXY

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Table IV. Comparison between the BID/ID⁻ and the BMN/MN⁻ Systems in 50% Me₂SO-50% Water at 20 °C

	BID/ID ⁻	BMN/MN ^{-a}	BMN/MN ⁻ BID/ID ⁻
$k_1, M^{-1} s^{-1}$	$7.23 \times 10^3 (3.13 \times 10^3)^d$	9.50×10^5	131 (304) ^e
k_{-1}, s^{-1}	$9.35 \times 10^{-3} (2.16 \times 10^{-2})^d$	6.52	697 (304) ^e
K_1, M^{-1}	$7.73 \times 10^5 (1.45 \times 10^5)^d$	1.45×10^5	0.188 (1.00) ^e
$pK_a^{o b}$	3.05	5.07	
$pK_a^{NucH^c}$	6.35	10.25	
$\log(k_0^{MN}/k_0^{ID})_{eq III}^f$	≈ 2.48		
$\log(k_0^{MN}/k_0^{ID})_{eq I}^g$	≈ 2.04		
$\log(k_0^{MN}/k_0^{ID})_{eq II}^g$	≈ 1.78		

^a From ref 2. ^b pK_a^o refers to T^o; in the BID/ID⁻ system $pK_a^o = pK_a^{K_1}$. ^c pK_a^{NucH} refers to pK_a of ID and MN, respectively. ^d Adjusted to K_1 of the BMN/MN⁻ system, based on $d \log k_1/d \log K_1 = -d \log k_{-1}/d \log K_1 = 0.5$; see text. ^e Using adjusted parameters for the BID/ID⁻ system. ^f k_0^{MN}/k_0^{ID} assumed to be equal to $k_1^{MN}/k_{-1}^{ID} = k_{-1}^{MN}/k_{-1}^{ID}$ using adjusted k_1^{ID} and k_{-1}^{ID} values; see text. ^g From ref 1.

moiety to CHXY⁻ and one from the formation of the C=O double bond:

$$\Delta G^*_0(\text{eq II}) = \Delta G^*_0(\text{XY})_{C-} + \Delta G^*_0(\text{O})_{C=O} \quad (13)$$

If we now add eq 12 and 13, we obtain

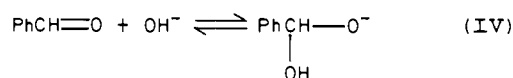
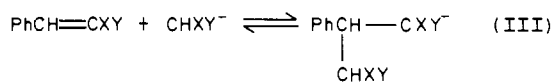
$$\Delta G^*_0(\text{eq I}) + \Delta G^*_0(\text{eq II}) = \Delta G^*_0(\text{XY}/\text{XY}) + \Delta G^*_0(\text{O}/\text{O}) \quad (14)$$

with

$$\Delta G^*_0(\text{XY}/\text{XY}) = \Delta G^*_0(\text{XY})_{C=C} + \Delta G^*_0(\text{XY})_{C-} \quad (15)$$

$$\Delta G^*_0(\text{O}/\text{O}) = \Delta G^*_0(\text{O})_{OH-} + \Delta G^*_0(\text{O})_{C=O} \quad (16)$$

It should be noted that thus far our formalism is not based on any particular model or assumption. However, at this point we introduce a Marcus-type assumption which stipulates that $\Delta G^*_0(\text{XY}/\text{XY})$ is a good approximation of the intrinsic barrier of reaction III, and that $\Delta G^*_0(\text{O}/\text{O})$ is a good approximation of the intrinsic barrier of reaction IV.



This is expressed by

$$\Delta G^*_0(\text{XY}/\text{XY}) \approx \Delta G^*_0(\text{eq III}) \quad (17)$$

$$\Delta G^*_0(\text{O}/\text{O}) \approx \Delta G^*_0(\text{eq IV}) \quad (18)$$

and eq 14 becomes

$$\Delta G^*_0(\text{eq I}) + \Delta G^*_0(\text{eq II}) \approx \Delta G^*_0(\text{eq III}) + \Delta G^*_0(\text{eq IV}) \quad (19)$$

It is now apparent that reactions III and IV take on the meaning of "pseudo-identity" reactions while eq I and II are the "pseudo-cross" reactions. Note that because there are no true identity reactions as in electron, proton, and methyl transfers, there are two different (pseudo) cross reactions rather than only one (authentic) cross reaction.

For a change from XY to X'Y' such as the change from the MN to the ID or the NO₂ system, we now obtain ($\Delta \Delta G^*_0(\text{eq IV}) = 0$)

$$\Delta \Delta G^*_0(\text{eq I}) + \Delta \Delta G^*_0(\text{eq II}) \approx \Delta \Delta G^*_0(\text{eq III}) \quad (20)$$

or

$$\log(k_0^{XY}/k_0^{X'Y'})_{eq I} + \log(k_0^{XY}/k_0^{X'Y'})_{eq II} \approx \log(k_0^{XY}/k_0^{X'Y'})_{eq III} \quad (21)$$

How well does eq 21 reproduce our results? For the MN/ID comparison we have $\log(k_0^{MN}/k_0^{ID})_{eq I} + \log(k_0^{MN}/k_0^{ID})_{eq II} \approx$

$1.86 + 1.78 = 3.64$ which is 1.16 log units larger than the experimental $\log(k_0^{MN}/k_0^{ID})_{eq III}$ of 2.48. For MN/NO₂ the corresponding ratios are $\log(k_0^{MN}/k_0^{NO_2})_{eq I} + \log(k_0^{MN}/k_0^{NO_2})_{eq II} \approx 4.20^{13} + 3.96^{13} = 8.16$ which is 2.44 log units higher than the experimental $\log(k_0^{MN}/k_0^{NO_2})_{eq III} \approx 5.70$.

Despite the fact that eq 21 overestimates $\log(k_0^{XY}/k_0^{X'Y'})_{eq III}$ for both comparisons, it is noteworthy that the experimental $\log(k_0^{XY}/k_0^{X'Y'})_{eq III}$ values are significantly larger than either $\log(k_0^{XY}/k_0^{X'Y'})_{eq I}$ or $\log(k_0^{XY}/k_0^{X'Y'})_{eq II}$, in qualitative agreement with the basic Marcus idea. Nevertheless, one wonders why the quantitative agreement is not better.

One possible factor for the lack of quantitative agreement is the significant experimental uncertainty in some of the ratios, particularly in $(k_0^{MN}/k_0^{ID})_{eq II}$,¹ $(k_0^{MN}/k_0^{NO_2})_{eq II}$,¹ and $(k_0^{MN}/k_0^{NO_2})_{eq III}$,¹³ which arise from uncertainty in equilibrium constants,¹³ and the relatively long extrapolations coupled with the arbitrary assumption that the Brønsted slopes can always be approximated by 0.5.¹

A second factor may be related to the criticism voiced by Ritchie,¹⁸ namely, the fact that eq III and IV are not true identity reactions. It would be interesting in this context to examine proton-transfer reactions involving the same type of activating substituents ((CN)₂, β-diketo, NO₂) and see whether the quantitative adherence to the Marcus stipulation that the intrinsic barrier of a cross reaction is the arithmetic mean of the two corresponding identity reactions is indeed better than what we observe here. It is noteworthy that there still exist only very few data of this kind for proton transfers.¹⁹

A third factor which is likely to play a role in some of our reactions is the large transition-state imbalances which are characteristic of reactions involving resonance-stabilized carbanions,⁷ particularly with nitronate ions.^{20,21} Such imbalances lead to substituent effects on the intrinsic barriers which cannot be accommodated by the original Marcus formalism.^{22,23} This is because the Marcus formalism is based on the description of the reaction coordinate by a single progress variable while reactions with imbalanced transition states need at least two variables (e.g., one for the formation of bonds, the other for the development of resonance) for an adequate description of the reaction coordinate.^{7,24,25} Grunwald²⁶ has recently suggested a possible way to deal with this problem.

A fourth factor may be the neglect of work terms in the Marcus equation.^{11a} These are commonly explicitly considered in electron-transfer reactions but usually incorporated into the intrinsic

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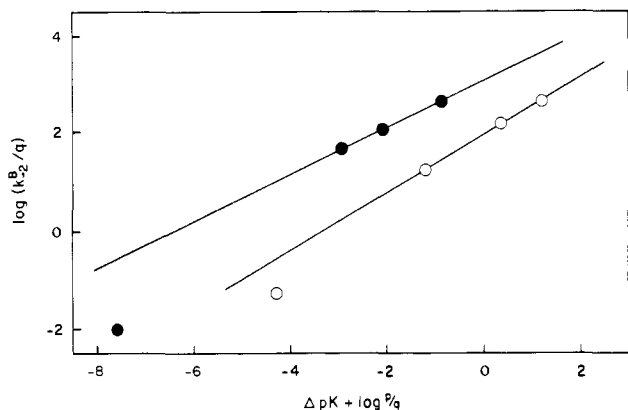
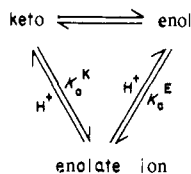


Figure 4. Brønsted plots for the deprotonation of the adduct $T_{ID}^0_{keto}$ (O) by water, Cl_2CHCOO^- , $CICH_2COO^-$, and $MeOCH_2COO^-$, and of ID (●) by water, $CICH_2COO^-$, $MeOCH_2COO^-$, and AcO^- ; $\Delta pK = pK_a^{BH} - pK_a^{CH}$.

barrier for other reactions.²⁷ We do not believe that this is an important factor, though.

Enol Formation: pK_a^K and pK_a^E . From Table III we see that pK_a^K of $T_{ID}^0_{keto}$ (Scheme I) is 3.3 units lower than the pK_a of the keto form of ID. This reflects the electron-withdrawing effect of the ID moiety. A similar comparison in the BMN/MN system shows that the adduct (T_{MN}^0) is 5.14 pK_a units more acidic than MN (Table IV). The larger effect in the BMN/MN⁻ system is probably the result of two factors: (a) a larger polar effect of the MN moiety²⁸ compared to the ID moiety;²⁹ (b) substantial delocalization of the negative charge into the oxygens in T_{ID}^- which renders the pK_a^K of $T_{ID}^0_{keto}$ less sensitive to polar effects.

The acidifying effect of the ID moiety on the enol form ($T_{ID}^0_{enol}$) is a relatively modest 1.16 pK_a units (Table III) and thus is much less than that on the keto form. According to the thermodynamic cycle



this means that the enolization constant, $K_E = K_a^K/K_a^E$ is much larger for the BID/ID adduct ($K_E = 0.204$) than for ID itself ($K_E = 1.48 \times 10^{-3}$).

(27) See, however, ref 25, and (a) Kreevoy, M. M.; Konasewich, D. E. *Adv. Chem. Phys.* **1971**, *21*, 241. (b) Kreevoy, M. M.; Oh, S.-W. *J. Am. Chem. Soc.* **1973**, *95*, 4805. (c) Albery, W. J.; Campbell-Crawford, A. N.; Curran, J. S. *J. Chem. Soc., Perkin Trans. 2* **1972**, 2206.

(28) $\sigma_1 = 0.55$ for $CH(CN)_2$.³⁰

(29) σ_1 for $HC(CO)_2C_6H_4$ is not known but may be estimated at ≤ 0.3 ; 0.3 would be three times the σ_1 value of 0.1 for CH_2COCH_3 ,³⁰ in analogy to σ_1 for $CH(CN)_2$ being three times σ_1 for CH_2CN .³⁰ Since in most cases σ_1 of CHX_2 is less than three times σ_1 of CH_2X ,³⁰ the factor of 3 is an upper limit.

(30) Exner, O. In "Correlation Analysis in Chemistry"; Chapman, N. B., Shorter, J., Eds.; Plenum Press: New York, 1978; p 439.

We attribute this large increase in the enolization constant mainly to intramolecular hydrogen bonding in $T_{ID}^0_{enol}$ as shown in Scheme I. Intramolecular hydrogen bonding is indeed a well-documented phenomenon in the stabilization of many enols.³¹ The electron-withdrawing effect of the ID moiety may be a contributing factor;³¹ in fact, the introduction of a phenyl group at the 2 position of ID increases the enol content to 2.4% in aqueous solution.³²

Rates of Proton Transfer. The rate constants for proton transfer are summarized in Table II. Figure 4 shows a Brønsted plot for the deprotonation of $T_{ID}^0_{keto}$ along with a similar plot for the deprotonation of ID¹⁰ by three carboxylate ions.³³ The Brønsted β -values are $\beta = 0.58 \pm 0.03$ for $T_{ID}^0_{keto}$, $\beta = 0.48 \pm 0.03$ for ID.

The Brønsted line for $T_{ID}^0_{keto}$ lies below that for ID; at $\Delta pK_a + \log(p/q) = 0$ the difference amounts to a factor of 12. We attribute the reduced proton-transfer rate for $T_{ID}^0_{keto}$ to a steric effect.

Experimental Section

Materials. 1,3-Indandione (Aldrich) was recrystallized from ethanol, mp 131–132 °C (130 °C).³⁴ Benzylidene-1,3-indandione was available from a previous study.¹ Chloroacetic acid was recrystallized from petroleum ether. Reagent grade Me_2SO was stored over 4A molecular sieves. All other materials were analytical-grade products which were used without further purification.

Kinetics. When measuring the rates of adduct formation, an acidic solution of 2×10^{-5} M BID was mixed in the stopped-flow apparatus with slightly basic *p*-cyanophenol buffers containing varying concentrations of ID. The excess of $[ID]_0$ over $[BID]_0$ was always at least 10-fold. Since ID^- also absorbs in the range of λ_{max} of BID (343 nm, $\epsilon 2.47 \times 10^4$ $M^{-1} cm^{-1}$) where the reaction was monitored, it was not possible to use $[ID]_0$ greater than 8×10^{-4} M.

For the pH-jump experiments the adduct, T_{ID}^- , was generated by mixing equimolar quantities of BID and ID in a small excess of KOH, giving a pH of ~ 9.2 after formation of T_{ID}^- . These solutions were quite stable for several days but were always used within 12 h after preparation. The pH jump was produced by adding an acidic buffer or an HCl solution to the T_{ID}^- solution, either in the stopped-flow apparatus (τ_1^{-1}) or a conventional spectrophotometer (τ_2^{-1}).

pH measurements were performed on mock solutions which simulated the stopped-flow experiments. For the slow reactions the pH was determined in the actual reaction solution.

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Registry No. ID, 606-23-5; ID^- , 19368-95-7; MN^- , 41470-37-5; BID, 5381-33-9; BMN, 2700-22-3; TIDO keto, 7421-80-9; TIDO enol, 98635-29-1; TID^- , 98635-30-4; AcO^- , 71-50-1; Cl_2CHCOO^- , 13425-80-4; H_3O^+ , 13968-08-6; $Cl_2CHCOOH$, 79-43-6; $CICH_2COOH$, 79-11-8; $MeOCH_2COOH$, 625-45-6; $CICH_2COO^-$, 14526-03-5; $MeOCH_2COO^-$, 20758-58-1; water, 7732-18-5.

Supplementary Material Available: Tables S1 and S2, kinetic data (3 pages). Ordering information is given on any current masthead page.

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