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ORIGINAL PAPER

Paradigms and paradoxes: Energetics of the oxidative cleavage of indigo and of other olefins

Aaron T. Frank · Adebogun Adenike · David Aebisher · Alexander Greer · Ruomei Gao · Joel F. Liebman

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Abstract Indigo is a unique organic compound in terms of its blue color and its multiple conjugated functional groups contained therein. We ask whether the enthalpy of its cleavage reaction into two isatin molecules reflects the novelty of either this color and/or the conjugated functionalities contained therein.

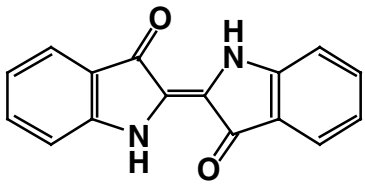
Keywords Blue color · Enthalpies of formation · Phase change and of reaction · Indigo · Oxidative cleavage · Carbonyl compounds · "Push–pull" olefins

Indigo, species **1**, is quite unique among organic compounds. It has a unique "eponymic" blue color and extensive historic provenance and importance in numerous cultures in both the Western and Eastern hemispheres (cf. the derivation of the word "indigo" from "India"). Both of these aspects, the color and the importance, have shown fading—there are now other dyes of diverse and popular hues that fill the rainbow-rich human-derived landscape of fabrics and other materials. The blue color slowly fades in objects of art and commerce colored by indigo as the central C=C bond is cleaved by air and other ubiquitous oxidants. Nonetheless, interest continues—we note our recent paper on the photooxidation chemistry of indigo [1].

A simple question regarding the oxidation of indigo relates the energetics of this process that forms the so-called (trivially named) isatin **2** to the corresponding oxidation of other olefins. More precisely, we may consider the generic process, Eq. (1),

$$RR'C = CRR' + [O] \rightarrow 2RR'CO \quad (1)$$

without regards to mechanism, rate or even the precise oxidizing agent used in this reaction.



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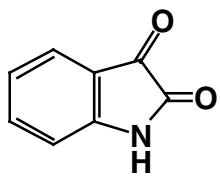

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We ask how "special" is indigo within this thermochemical context; is the blue color accompanied by a likewise surprising oxidation enthalpy? After all, indigo is structurally unique in its multiple conjugated functional groups contained therein: it is simultaneously an diaminoalkene as well as a 2-butene-1,4-dione as well as a "push–pull" enaminoketone. Each of these substructures is quite rare in the thermochemical literature, indeed simple enamines and α,β-unsaturated ketones (enones) are underrepresented therein: the decade-old reviews Refs. [2] and [3] respectively have preciously few updating examples, e.g., 1,1-diamino-2,2-dinitroethylene [4] and tetrakis(dimethylaminoethylene) [5], α-methyl and ethylacroleins [6], α-methylcinammaldehyde [7] and both 2-cyclopentenone and 2-cyclohexenone [8].

A. T. Frank · A. Adenike · D. Aebisher · A. Greer
Department of Chemistry, Graduate Center and The City University of New York (CUNY), Brooklyn College, Brooklyn, NY 11210, USA
e-mail: agreer@brooklyn.cuny.edu

R. Gao
Department of Chemistry, Jackson State University, Jackson, MS 39217, USA

J. F. Liebman (✉)
Department of Chemistry and Biochemistry, University of Maryland, Baltimore County, Baltimore, MD, 21250 USA
e-mail: jliebman@umbc.edu

Tables 1 and 2 present the enthalpies of reaction for a collection of acyclic olefins (arranged by the Hill sort scheme used in the formula index of Chemical Abstracts) so chosen to ignore effects from aromatic or antiaromatic rings. We explicitly give the enthalpies of formation and accompanying references for the reactant olefin and the carbonyl compound (l ≡ liquid, s ≡ solid): Table 1 is for gas-phase olefin and carbonyl compound while Table 2 is correspondingly for condensed-phase species. More precisely, we explicitly consider reaction (2) and its enthalpy, as to ignore the enthalpy of formation of the oxidant because it is now precisely 0.0 kJ/mol. (We note now, however, that the relative reaction enthalpies are indifferent to the choice of oxidant as long as the same is used for all reactions, whether it be singlet or triplet diatomic oxygen, ozone, superoxide or some other reagent of interest or practical efficacy.)

$$RR'C = CRR' + O_2 \rightarrow 2RR'CO \qquad (2)$$

We express indifference as to the (*E*)- and (*Z*)-stereochemistry of the double bond and explicitly consider both; thermochemical differences are generally relatively small. All unreferenced enthalpies of formation are from Ref. [9]. Sometimes, we interrelate enthalpies of formation of a liquid and the corresponding gaseous species by the enthalpy of fusion data from Ref. [10]. Likewise, enthalpies of formation of solids and gases are interrelated by enthalpies of sublimation from Ref. [11] while those of liquids and solids are interrelated with enthalpies of vaporization from Ref. [12]: we only explicitly cite the source of the enthalpy of formation of the condensed phase in these cases. In all cases of these uses of phase change enthalpies, should the idealized value at 298 K not be archivally given (cf. Refs. [10–12]), we do not make any temperature corrections to this standard temperature. We now acknowledge to the reader of our current preference of solid over liquid phase data since the solid state is the "natural" phase for indigo, the species of explicit, if not also primary, interest of this study. Liquid phase indigo, whether the melted solid, or in solution is ignored here—indigo is sparingly soluble in DMSO ($\sim$0.7 mM) and other solvents such as $CHCl_3$, CH_2Cl_2, CH_3CN, and CH_3OH ($<$ 0.1 mM) [1]. (This suggests that indigo will be hard to purify and so compromises the reliability of combustion calorimetry experiments.)

As a gas-phase process, reaction (2) shows a wide range of exothermicities. In general, those species that have π-electron donating substituents (amino, halo, thio, hydroxy) have relatively large reaction exothermicities, $\geq$ 400 kJ/mol. By contrast, those species that have π-electron withdrawing substituents (most notably cyano groups) have comparatively much smaller reaction exothermicities, ca. 250 kJ/mol. Sensibly interpolating species with rather milder π-donating substituents (alkyl and aryl) have intermediate (ca. 325 kJ/mol) values of exothermicities. We take the enthalpy of formation of solid indigo of $-$ 134 kJ/mol from Ref. [34], its sublimation enthalpy of 136 (at 577 K, thermally uncorrected), and that of the cleavage product, isatin in its gas phase, $-$ 133.0 $\pm$ 5.6 kJ/mol from Ref. [35]. Indigo, the "star of our show," has a reaction exothermicity to form its corresponding carbonyl compound, isatin, of 270 kJ/mol. In that the excuse of no substituents cannot be made (hydrogen is generally anomalous, and so the result for ethylene itself is atypical), we conclude that the net effect of the 2NH and 2CO groups in gas-phase indigo is net π-electron withdrawal.

As a condensed-phase process, reaction (2) again shows a wide range of exothermicities. In general, those species that have π-electron donating substituents (amino, halo) have relatively large reaction exothermicities, $\geq$ 430 kJ/mol. By contrast, species that have π-electron withdrawing substituents (most notably cyano, carboxyl groups) have comparatively much smaller reaction exothermicities, ca. 240 kJ/mol. We use the above-cited value of $-$ 134 kJ/mol for the enthalpy of formation of solid indigo [34] along with the value of $-$ 251.8 $\pm$ 2.4 kJ/mol for solid isatin [35]. We find indigo, the "star of our show," has a reaction endothermicity of 370 kJ/mol, a value quite similar to that of alkyl and arylated olefins. From this, we conclude that the net effect of the 2NH and 2CO groups in solid-phase indigo is a small amount of net π-electron donation.

Admittedly, this contradicts the earlier enunciated result for the gaseous species: even a plausible thermal correction as made using the various correction estimation equations in Ref. [11] fail to ameliorate this. We have currently no resolution for this—perhaps there is an error in the measured enthalpies of formation and/or of phase change for indigo. The former value is confounded by its antiquity—young, perhaps, compared to that of the species but more precisely, the experiments cited now over 110 years old and techniques of measurement and of compound purification were generally poorer then than now. We also note that the temperature associated with the latter measurement, 577 K, is much hotter than for other phase change enthalpies of interest to us in the current paper. Is it valid here to neglect the thermal correction for this species, or "merely" estimate it? It does not seem particularly plausible that indigo and the corresponding carbonyl compound have sublimation enthalpies differing by only ca. 18 kJ/mol. It is to be acknowledged that the enthalpy of formation of isatin chronicled by our archival source as part of Ref. [34] is $-$ 268.2 $\pm$ 3.7 kJ/mol, some 17 kJ more negative than in the contemporary reference [35], suggesting this substance, and *a fortiori* indigo, are problematic species for calorimetrist. We await the remeasurement of the enthalpy of formation of indigo, and may we add its enthalpy of sublimation as well: these will not be easy measurements but we feel rewarding and so recommended.

Table 1 Enthalpy of oxidation reaction (2) for gas-phase reactants and products, where we identify this process as an example reaction (1) with O_2 as the explicitly stated oxidant

Formula	Name	ΔH_f° (olefin)	Ref.	ΔH_f° (carbonyl)	Ref.	$-\Delta H_r$ (2)
C_2Cl_4	Tetrachloroethylene	− 24.2 ± 4.0	[13]	− 219.1 ± 0.5	[9]	427.5
C_2F_4	Tetrafluoroethylene	− 658.9 ± 4.9	[9]	− 624	[14]	589
$C_2H_2Cl_2$	(*E*)-1,2-Dichloroethylene	− 0.5 ± 2.0	[13]	− 192.7	[1]	385.4
$C_2H_2Cl_2$	(*Z*)-1,2-Dichloroethylene	− 3.0 ± 2.0	[13]	− 192.7	[15]	382.9
$C_2H_2I_2$	(*E*)-1,2-Diiodoethylene	207.4 ± 0.8	[9]	− 66.2	[15]	339.8
$C_2H_2I_2$	(*Z*)-1,2-Diiodoethylene	207.4 ± 0.8	[9]	− 66.2	[15]	339.8
C_2H_4	Ethylene	52.5 ± 0.3	[9]	− 108.6 ± 0.5	[9]	269.7
$C_2H_4O_2$	(*Z*)-Ethene-1,2-diol	− 316	[16]	− 378.7 ± 0.5	[9]	441.6
$C_4H_2N_2$	Fumaronitrile	340.2 ± 1.8	[9]	26 ± 20	[17]	288
$C_4H_2N_2$	Maleonitrile	340	[a]	26 ± 20	[17]	288
C_4H_8	(*E*)-2-Butene	− 11.4 ± 1.0	[9]	− 166.1 ± 0.5	[9]	320.8
C_4H_8	(*Z*)-2-Butene	− 7.1 ± 1.0	[9]	− 166.1 ± 0.5	[9]	325.1
C_6H_8	(*E*)-1,3,5-Hexatriene	165 ± 3	[19]	− 69 ± 10	[20]	303
C_6H_8	(*Z*)-1,3,5-Hexatriene	172 ± 3	[19]	− 69 ± 10	[20]	296
C_6H_8	(*E*)-2,3,4-Hexatriene	265	[21]	− 81 ± 15	[b]	427
C_6H_8	(*Z*)-2,3,4-Hexatriene	265	[21]	− 81 ± 15	[b]	428
C_6H_{12}	Tetramethylethylene	− 68.1 ± 1.1	[9]	− 217.1 ± 0.7	[9]	366.1
C_6H_{12}	(*E*)-3-Hexene	− 49.0	[23]	− 185.6 ± 0.8	[9]	322.2
C_6H_{12}	(*Z*)-3-Hexene	− 45.3	[23]	− 185.6 ± 0.8	[9]	325.9
C_6N_4	Tetracyanoethylene	705.0 ± 6.1	[9]	247.5 ± 6.4	[9]	212.5
C_8H_{12}	(*E*)-2,6-Dimethyl-1,3,5-hexatriene	95.8	[24]	− 106.4 ± 2.0	[6]	308.6
C8H16	(*E*)-4-Octene	− 93.5	[25]	− 204.8 ± 1.4	[9]	316.1
C8H16	(*Z*)-4-Octene	− 90.3	[25]	− 204.8 ± 1.4	[9]	319.3
$C_{10}H_{24}N_4$	Tetrakis(dimethylamino)ethylene	132.9 ± 2.0	[5]	− 205.6 ± 1.1	[25]	544.1
$C_{12}H_{18}$	(*E*)-Bis(2-cyclohexenylidene)[c]	91.2	[21]	− 121.9 ± 3.0	[8]	335
$C_{12}H_{18}$	(*Z*)-Bis(2-cyclohexenylidene)[c]	92.5	[21]	− 121.9 ± 3.0	[8]	336
$C_{14}H_{18}$	*cis*-Stilbene[d]	252.3 ± 1.3	[9]	− 36.7 ± 2.8	[9]	325.7
$C_{14}H_{18}$	*trans*-Stilbene[d]	236.1 ± 1.2	[9]	− 36.7 ± 2.8	[9]	309.5
$C_{16}H_{12}O_2$	1,4-Diphenyl-2-butene-1,4-dione	− 5	[e]	− 136	[f]	267
$C_{16}H_{16}S_2$	(*E*)-Bis(benzylthio)ethylene	333	[g]	− 39	[h]	411
$C_{16}H_{16}S_2$	(*Z*)-Bis(benzylthio)ethylene	346	[g]	− 39	[h]	411
$C_{26}H_{20}$	Tetraphenylethylene	448.9	[9]	50.9 ± 2.4	[28]	347.1
$(CHCH)_n$	Polyacetylene	57	[i]	212.0 ± 0.7	[9]	269

Note. If a reference is not given explicitly for a value, a footnote is denoted in the appropriate column and details are provided with relevant input citations given as well.

[a] This value was obtained by combining the archival enthalpy of formation of fumaronitrile and the assumption that the entropies of formation of these two isomers are very nearly the same; this is derived from the observation (in Ref. [18]) that equilibration of these two species results in a 46:54 ratio, so very nearly 1:1, and the plausible assumption that the entropies of the isomers are essentially the same.

[b] This value is the consensus of the values suggested by Refs. [22a–c].

[c] There are three methylene groups separating the π terminus of the "cyclohexenylidene" substitutent from the central double bond. Accordingly from the electronic vantage point, this group is very much like that of a pair of vinyl and alkyl substituents, and hence the current species may be considered acyclically substituted.

[d] We considered this species acyclic because the phenyl group may be considered a univalent substituent analogous to all of the others in this paper.

[e] We summed the archival enthalpy of formation of the solid species with the average enthalpy of sublimation of other related diones, namely a set of annelated quinones; all input data is from Ref. [9].

[f] We averaged the archival enthalpy of formation of gas-phase glyoxal with the new value for its diphenylated derivative (benzil) from Ref. [26].

[g] We approximated the enthalpy of sublimation of this species by the archival value (Ref. [9]) of that of 2,5-diphenyl-1,2-dithiin, a species of very nearly the same composition as the species of interest.

[h] We estimated this value by assuming thermoneutrality for the transesterification reaction $C_6H_5CH_2SH + HC(O)SC_2H_5 \rightarrow C_2H_5SH + HC(O)SCH_2C_6H_5$; the enthalpy of formation of ethyl thiolformate is taken from Ref. [27].

[i] This value was obtained from the analysis of Ref. [29]

Table 2 Enthalpy of oxidation reaction (2) for condensed-phase reactants and products, where we identify this process as an example reaction (1) with O_2 as the explicitly stated oxidant

Formula	Name	ΔH_f° (olefin)	Ref.	ΔH_f° (carbonyl)	Ref.	$-\Delta H_r$ (2)
C_2Cl_4 (l)	Tetrachloroethylene	−74.8	[13]	−240.3	[9]	406
$C_4H_4O_4$ (s)	Fumaric acid	−811.7 ± 0.7	[9]	−527	[a]	242
$C_4H_4O_4$ (s)	Maleic acid	−789.4 ± 0.8	[9]	−527	[a]	265
C_4H_8 (s)	(*E*)-2-Butene	−42.1	[9]	−196.2	[9]	350.3
C_4H_8 (s)	(*Z*)-2-Butene	−37.1	[9]	−196.2	[9]	355.3
C_6H_8 (l)	(*E*)-1,3,5-Hexatriene	123.1	[32]	−120	[33]	363
C_6H_{12} (l)	(*E*)-3-Hexene	−82.1 ± 0.9	[23]	−215.6 ± 0.9	[9]	349.1
C_6H_{12} (l)	(*Z*)-3-Hexene	−78.1 ± 0.9	[23]	−215.6 ± 0.9	[9]	353.1
C_6H_{12} (s)	Tetramethylethylene	−111.4	[9]	−254.1	[9]	396.8
C_6N_4 (l)	Tetracyanoethylene	648.7	[9]	211.5 ± 5.4	[9]	225.6
C_8H_{16} (l)	(*E*)-Di-isopropylethylene	−159.2 ± 2.9	[9]	−247.3 ± 1.5	[9]	335.4
C_8H_{16} (l)	(*Z*)-Di-isopropylethylene	−151.0 ± 3.7	[9]	−247.3 ± 1.5	[9]	343.6
$C_{10}H_{24}N_4$ (l)	Tetrakis(dimethylamino) ethylene	79.1 ± 2.0	[5]	−262.2 ± 1.1	[25]	603.5
$C_{14}H_{12}$ (l)	*cis*-Stilbene	183.3 ± 1.5	[9]	−87.0 ± 2.0	[9]	357.3
$C_{14}H_{12}$ (s)	*trans*-Stilbene	136.9 ± 1.1	[9]	−96.3	[9]	329.5
$C_{26}H_{20}$ (s)	Tetraphenylethylene	311.5 ± 1.4	[9]	−42.2 ± 1.0	[28]	395.9

Note. (l) and (s) refer to liquid and solid respectively. (If a reference is not given explicitly for a value, a footnote is denoted in the appropriate column and details are provided with relevant input citations given as well).

[a]The enthalpy of formation of the relevant carbonyl compound, glyoxylic acid, is not −835.5, cf. Ref. [30]. This value is, in fact, for the hydrate. If we assume the same condensed-phase enthalpy of hydration as found for another acetaldehyde derivative with electron withdrawing substituents namely trichloroacetaldehyde (23 kJ/mol from Ref. [31]) and the archival enthalpy of formation of liquid water, we obtain an enthalpy of formation of anhydrous glyoxylic acid of −527 kJ/mol. It is this value we use and report here.

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