Title

Is Electron Transfer a Step in the Nitration of Reactive Aromatics?

Journal

The Journal of Organic Chemistry

ISSN

0022-3263

Author

Perrin, Charles L

Publication Date

2026-02-17

DOI

10.1021/acs.joc.5c03251

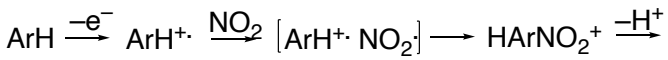
Peer reviewed

Is Electron Transfer a Step in the Nitration of Reactive Aromatics?

Charles L Perrin*
Department of Chemistry, University of California—San Diego, La Jolla, CA 92093-0358

cperrin@ucsd.edu

TOC Graphic

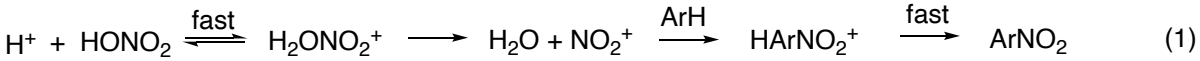


Abstract

Controlled-potential electrolysis of a mixture of NO_2 and naphthalene, at an applied potential capable of oxidizing naphthalene but not NO_2, produces a mixture of nitronaphthalenes. The ratio of 1-nitronaphthalene to 2-nitronaphthalene is 10.2 ± 1, the same as the 10.9 ± 1 produced in the direct nitration of naphthalene with $HNO_3 + H_2SO_4$. The observation that the same mixture is formed by the two routes is taken as evidence that a radical pair is involved not only in the electrochemical synthesis but also in the direct nitration. This requires that electron transfer from aromatic to NO_2^+ be sufficiently fast to compete with C-N bond formation. Moreover, formation of a radical pair is presented as the explanation for the high intramolecular selectivity of nitration, contrasting with a lack of intermolecular selectivity. This full paper presents the experimental details of a Communication to the Editor published in JACS in 1977, along with a review of experimental and computational assessments both in favor and in opposition to that Communication.

Introduction

For many years aromatic nitration was considered one of the most fully understood organic reactions in solution. According to classic studies,[1] the rate-limiting step for aromatics ArH more reactive than toluene is the formation of the nitronium ion, NO_2^+, by water loss from protonated nitric acid. This then rapidly adds to the aromatic, to form the intermediate $HArNO_2^+$, which finally loses a proton to form the nitrated aromatic $ArNO_2$. This mechanism is summarized in eq 1.



(1)

The rate-limiting step is the formation of NO_2^+, which then adds to a sufficiently reactive aromatic in an encounter-limited step.[2] Consequently there is no substrate selectivity in the attack of NO_2^+. Despite this low substrate selectivity there is high positional selectivity, quite comparable to that seen with selective electrophiles. For example, nitration of 1,2,4-trimethylbenzene produces 5-nitro and 6-nitro products in a 9:1 ratio, consistent with the typical ortho/para directing effects of two methyls versus one.[3]

To reconcile this contrast between low intermolecular selectivity and high intramolecular selectivity, Perrin proposed that the $ArH{\cdot}NO_2^+$ encounter complex undergoes rapid electron

$$NO_2^+ + ArH \xrightarrow[\text{controlled}]{\text{encounter-}} \left[ArH\ NO_2^+ \right] \xrightarrow[\text{(fast)}]{e^- \text{ transfer}} \left[ArH^{\pm\cdot}\ NO_2\cdot \right] \longrightarrow HArNO_2^+ \xrightarrow{-H^+} \quad (2)$$

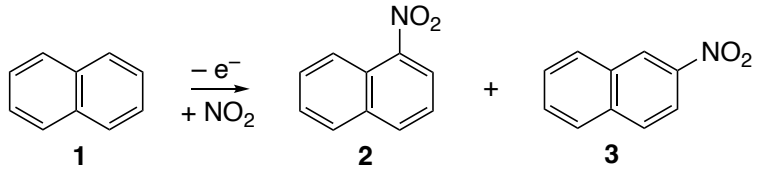
transfer, as in eq 2, to form a radical pair $ArH^{+\cdot}{\cdot}NO_2\cdot$ that then collapses to the σ-adduct, which finally deprotonates.[4] Although the encounter is unselective, radical-pair collapse to $HArNO_2^+$ could depend on spin density and be more selective. It must be acknowledged that electron transfer was proposed quite early as involved in aromatic nitration.[5]

In support of this proposal Perrin measured the anodic half-wave potentials for oxidation of NO_2 and of several aromatics in acetonitrile as solvent. The data show that electron transfer to NO_2^+ is thermodynamically favorable from all aromatics more reactive than toluene.

To test the proposal of eq 2 Perrin prepared the radical pair $ArH^{+\cdot}{\cdot}NO_2\cdot$ by an independent procedure, namely oxidation of the aromatic and encounter with $NO_2\cdot$ (eq 3).

$$ArH \xrightarrow{-e^-} ArH^{+\cdot} \xrightarrow{NO_2} \left[ArH^{+\cdot}\ NO_2\cdot \right] \longrightarrow HArNO_2^+ \xrightarrow{-H^+} \quad (3)$$

Specifically, a mixture of naphthalene (**1**) and NO_2 (in equilibrium with N_2O_4) was subjected to controlled-potential electrolysis at an applied potential capable of oxidizing naphthalene but not NO_2. This procedure produced a mixture of nitronaphthalenes (eq 4). The ratio of 1-nitronaphthalene (**2**) to 2-nitronaphthalene (**3**) was 10.2 ± 1, within experimental error the same as the 10.9 ± 1 produced in the direct nitration of naphthalene with $HNO_3 + H_2SO_4$. The observation that the same mixture is formed by the two routes was taken as evidence that the radical pair is involved not only in the electrochemical synthesis but also in aromatic nitration.



1 **2** **3** (4)

The purpose of this article is to present the experimental details of that original procedure, to respond to criticisms of that study, and to summarize more recent research into the mechanism of aromatic nitration. This reaction is claimed to be the most studied and most important transformation among industrial processes,[6] so its full understanding is a worthy goal.

Experimental Procedure

Naphthalene, 1-nitronaphthalene, 2-nitronaphthalene, and electrolytes were commercial products, used without further purification. Nitrogen dioxide (N_2O_4) was prepared by pyrolysis of $Pb(NO_3)_2$. Acetonitrile was reagent-grade, dried over Al_2O_3 that had been heated to 330 ºC, but with no further precautions against water. The elution solvent for HPLC was 4-6% reagent CH_2Cl_2 in redistilled reagent hexanes.

Controlled-potential electrolyses were carried out with a three-electrode Heath EUW-401 Polarography System. The anode was a square of platinum gauze, the reference electrode was a silver wire, in 0.1 M $NaClO_4$ + 0.01 M $AgClO_4$, and the counterelectrode was a square of silver foil. An unglazed porcelain thimble served as cell divider. Electrolyses were carried out at 20-22 ºC on 100 mL of a stirred solution 2.5 mM in naphthalene, 5 mM in N_2O_4, 0.1 M in $NaClO_4$, and 0.01 M in $AgClO_4$. At an applied potential of 1.30 V the current was 1 ma, close to the maximum for that apparatus. In a typical experiment electrolysis was continued for 95 minutes (sufficient to electrolyze < 25% of the naphthalene, although the yield of nitronaphthalenes was lower, owing to formation of other oxidation products). Without electrolysis, but in the presence of 2 mM H_2SO_4, no nitration occurred during 95 minutes (less than 5% of that upon electrolysis). This is an important control experiment, as requested.[7]

Nitrations of naphthalene were carried out with various mixtures of 0.5-2.0 M HNO_3, 0.5-5.0 M H_2SO_4, and 0.1-0.4 M urea, in CH_3CN containing 10-20% water. Product ratios were independent of the composition of the mixture, except when the urea was replaced by $NaNO_2$, so that nitration proceeded by nitrosation.

Electrolysis analytes or nitration mixtures were quenched with water and extracted with CCl_4. The CCl_4 layer was washed with water, dried over CaO, prechromatographed over silica, and analyzed on a Waters H6000a HPLC equipped with a Microporosil column and an integrating recorder. The HPLC has the further advantage that its UV detector is more sensitive to the minor product 2-nitronaphthalene than to 1-nitronaphthalene.

Results

Table 1 lists the 1-nitro/2-nitro ratio from selected nitrations of naphthalene under various conditions. Much of this research was summarized by Eberson and Radner in an authoritative review that criticized the original proposal of electron transfer.[8] Moreover, they obtained much lower yields of nitronaphthalenes from electrolysis at 5 ºC than at 25 ºC.[9] This was taken as evidence that a homogeneous process catalyzed by anodically generated H^+ was responsible for the major part of product formation, rather than the electrolysis.

Table 1. 1-Nitro/2-nitro ratio from nitrations of naphthalene.

Process	Conditions	[α]/[β]	Ref.
electrolysis	V_{app} = 1.30 V	10.2±1.0	4,*
HNO_3+H_2SO_4+urea	aqueous CH_3CN	10.9±1.0	4,*
HNO_3+H_2SO_4+$NaNO_2$	aqueous CH_3CN	21.6±1.0	*
NO_2BF_4	CH_3NO_2	12	7
N_2O_4	CH_3CN	24	7
nitration by NO_2·	CH_3CN	25±3	9
electrolysis[a]	CH_3CN	20±3[b]	9
NO_2BF_4	CH_3CN	11±1	9
$(ArH)_2^{+\cdot}$ + N_2O_4	–25 ºC, CH_2Cl_2	43±3	10
electrolysis[a]	CH_3CN	17±3	11

*This manuscript. [a]Current yield > 100%. [b]Temperature-dependent.

Discussion

This section is organized to first present all the evidence consistent with an electron-transfer step and then all the evidence adduced as contradictory to the electron-transfer pathway. The contradictory evidence of Eberson is addressed separately at the end. We here first cite reviews that attempt to make sense of this controversy: two authoritative reviews by Ridd,[12,13] one more in Portuguese,[14] another translated from the Russian,[15] and a review of recent synthetic procedures for aromatic nitration, along with mechanistic considerations.[16]

The necessity for an additional step in the nitration process was provided early by the observation that the intermolecular selectivity between toluene and benzene is low, less than twofold, whereas the intramolecular selectivity is high, affording only 2.8% of *m*-nitrotoluene, corresponding to a partial rate factor m_f of only 0.14.[17] These observations together imply the paradoxical conclusion that the meta position of toluene (and of other monoalkylbenzenes) is even less reactive than a single benzene position. Indeed it was noted that nitrations with nitronium salts are "anomalous"; they are among the very few electrophilic aromatic substitutions for which the partial rate factors deviate from the correlation between log p_f^{Me} and lg(p_f^{Me}/m_f^{Me}), consistent with separate steps determining intermolecular and intramolecular selectivities.[18] Olah thus concluded that those observations are “inconsistent with any mechanism in which the individual nuclear positions compete for the reagent”.[19] It was then proposed that the first step of the reaction is the formation of a weakly bound π complex, the step responsible for substrate selectivity, whereas the positional selectivity is exerted in the conversion into the separate ortho, meta, and para sigma complexes, thereby allowing for a higher positional selectivity.

Olah and coworkers presented a more ambiguous appraisal of the role of electron transfer, referring to a "first intermediate" but also accepting that there are two intermediates prior to the σ complex, the first of which determines substrate selectivity and the second of which determines the positional selectivity.[20] Subsequent multi-configurational SCF calculations provided support for electron transfer to NO_2^+ from the more easily oxidizable aromatics.[21] The three intermediates were thus specified in sequence as a π complex, a radical pair, and the arenium ion.

Further support for a mechanism including an electron-transfer step was provided by a study of the reactions of polyalkoxylated benzenes and of naphthalene with *N*-nitropyridinium ion or tetranitromethane.[22] Such conclusions have been reviewed by Kochi.[23] In further support of the electron-transfer step, laser-flash photolysis of the charge-transfer complex between dialkoxybenzenes and $C(NO_2)_4$ produced the same mixture of products as did the direct nitration of those aromatics,[24] and so did nitration of naphthalene with *N*-nitropyridinium ions.[25] Such studies on charge-transfer nitrations of aromatic hydrocarbons were shown to proceed via a [$ArH^{\cdot+}$ $NO_2^{\cdot}$ Py] complex.[26] These studies have been further reviewed by Kochi.[27]

Comparison with the nitration of 1,8-dimethylnaphthalene with NO_2BF_4 in 1:1 CH_3CN:CH_2Cl_2 led to the conclusion that the reaction could proceed via electron transfer, despite the high energy of activation for the distortion change of the NO_2.[28] Further support for the electron-transfer process was obtained from the unusual regioselectivity in the dinitration of 1,2 and 1,4-dialkoxybenzenes.[29] Still another electron-transfer mechanism was proposed for the

nitration of aromatics using NO_2· as initiator, followed by encounter of the radical cation with another NO_2·.[30]

Among the articles denying electron transfer are the following based on observation or lack of observation of chemically induced dynamic nuclear polarization (CIDNP): According to the extent of ^{15}N nuclear polarization, electron transfer makes "a small yet significant contribution" in the nitration of naphthalene.[31] In support of the involvement of electron transfer in nitration of naphthalene with NO_2^+ in CF_3COOH-CH_3NO_2, ^{15}N NMR detected nuclear polarization, consistent with electron transfer between the reactants.[32] Still another study using ^{15}N CIDNP concluded that electron transfer is not involved.[33] However, it must be recognized that CIDNP is likely to be weak even following electron transfer inasmuch as the radical pair does not undergo separation but collapses immediately to the nitro adduct.

The UV spectrum of a 1:1 H_2SO_4/HNO_3 mixture containing 0.02 M benzene, recorded 4 minutes after mixing the reactants, showed an absorbance at 320 nm, attributed to a charge-transfer complex.[34a] However, DFT/M06-2X computations on the nitration of benzene showed no evidence for electron transfer in solution. Population analysis predicted a large amount of electron transfer from benzene to NO_2^+ in the gas phase. However, in solution, when association with a counterion is considered, the distance between the benzene pi-system and the NO_2^+ is too great to permit any significant charge transfer. That study was affirmed in a subsequent review article that concluded that the reaction proceeds from the pi complex via a transition state directly to the arenium ion intermediate.[35] Moreover, the 320-nm absorbance was subsequently rejected as attributable to a reaction complex.[34b] However, it must be recognized that benzene may not be sufficiently electron-rich to donate an electron to NO_2^+.

A more complicated system is the controlled-potential electrolysis of a mixture of naphthalene and $NaNO_2$ in acetonitrile, at a potential where both substrates are oxidized.[36] Cyclic voltammetry of such a mixture verified that both naphthalene and NO_2^- could be oxidized, whereupon the NO_2· reacted with the naphthalene radical cation. According to glc, the resulting nitronaphthalene was 98% 1-nitro. Electrolysis in aqueous solution does not lead to nitronaphthalenes, but they are formed when the electrolysis was carried out in in the presence of the nonionic surfactant Brij35.[37] The 1-nitro/2-nitro ratio was 16, with an increased percentage of 2-nitro that was attributed to a micellar effect.

According to potentiometric studies in sulfolane, electron transfer from naphthalene and other reactive aromatics to NO_2^+ is thermodynamically favorable but too slow to be involved in the nitration reaction.[38] The same conclusion was reached for reaction in nitromethane as solvent.[39]

Response to Eberson

A formidable objection to the 1977 proposal by Perrin[4] was expressed by Eberson, Jönsson, and Radner (EJ&R),[9] They purported to repeat the controlled-potential electrolysis of naphthalene in acetonitrile in the presence of N_2O_4. As included in Table 1, they obtained an α:β ratio of 20±3, significantly different from the 10.2±1.0 obtained by Perrin. Moreover, the yields

were > 100% and they were temperature-dependent, meaning that not all the product was produced electrochemically.

A key to this discrepancy is that EJ&R maintain that "the nitration observed in the electrolysis experiment was due to a homogeneous reaction between naphthalene and nitrogen dioxide, catalyzed by anodically generated hydrogen ion". That is indeed likely under the conditions of EJ&R, using 0.2 M naphthalene and 0.2 M NO_2, But those concentrations are nearly two orders of magnitude higher than the 2.5 mM naphthalene and 5 mM N_2O_4 used by Perrin. At those higher concentrations and higher current densities, it is indeed likely that anodically generated H^+ reacts with N_2O_4 to produce NO^+, which is the electrophile that carries out the nitration. (Indeed, Eberson and Radner further found that polycyclic aromatics could be nitrated with N_2O_4 in CH_2Cl_2, but that acid catalysis is necessary for less reactive aromatics, including naphthalene.[40]) That is why EJ&R's α:β ratio was 20±3, consistent with the 21.6±1.0 characteristic of nitration via nitrosation included in Table 1. (In another experiment Eberson and Radner reacted solid $C_{10}H_8^{\prime+}$ PF_6^- with N_2O_4 in CH_2Cl_2 at –45 to –25°, to produce nitronaphthalenes with an α:β ratio of ~40,[41] again characteristic of nitration via nitrosation.) Therefore it was concluded that the radical recombination cannot be involved as an elementary step in the nitration mechanism.

In contrast, Perrin's current was only 1 ma, sufficient to electrolyze < 25% of the 2.5 mM naphthalene, but apparently not sufficient to produce significant H^+. Indeed, Boughriet and coauthors expressed caution regarding the elucidation of the mechanism of nitration in the presence of N_2O_4.[42] They noted that it is not easy to eliminate nitration by NO^+. It is unfortunate that EJ&R used such high concentrations of reactants and such high current densities, but their analysis was constrained to their higher concentrations because they lacked the HPLC instrumentation necessary for product analysis from a microelectrolysis.[43] Therefore they did not repeat Perrin's experiment, contrary to their claim. It is therefore asserted that that experiment documents Perrin's conclusion that the same product mixture is obtained electrochemically as by direct nitration, strong evidence for the involvement of electron transfer in nitration of reactive aromatics.

Survey of Computations

A key question is whether electron transfer can occur rapidly enough from the aromatic to NO_2^+. For aromatics more electron-rich than toluene this electron transfer is thermodynamically favorable, although the calculation of relative stability is sensitive to the local polarity. A nonpolar medium favors positive charge to be delocalized over an aromatic ring rather than localized on the nitrogen of NO_2^+, whereas the presence of a counterion could reverse that preference. However, the key question is whether electron transfer is fast enough to occur during the lifetime of the encounter pair. The barrier to electron transfer may be substantial, because NO_2^+ is linear whereas $NO_2^{\cdot}$ is bent, with an O-N-O angle of 134º.[44] Therefore the linear NO_2^+ must bend in order to accept the electron, a distortion that imposes an activation energy on the electron transfer.

In the Supporting Information the computational results are surveyed chronologically, but with those that deny the electron transfer before those that support it.

Conclusions

The key experimental evidence for electron transfer from aromatic to NO_2^+ is the observation that the same α:β product ratio is observed in the electrolysis of naphthalene in the presence of NO_2 as in the direct nitration of naphthalene with NO_2^+. The inability of Eberson, Jönsson, and Radner to repeat this electrochemical result is then attributable to the fact that they did not work on microscale. Consequently the acid generated under their conditions was sufficient to promote nitration via nitrosation

Extensive calculations, largely on benzene and toluene, both deny and support electron transfer in nitration of reactive aromatics, as summarized in the Supporting Information. It may be noted that the average date of publications that deny electron transfer is 2002, whereas that of those that support electron transfer is 2006. To the extent that later calculations use more sophisticated technology, this comparison suggests, albeit weakly, that a more sophisticated technology is necessary to document electron transfer.

Those more recent calculations that support electron transfer have encouraged the submission of this article so as to more fully document the evidence of that communication from nearly fifty years ago. Of course, further highest-level calculations on nitration of naphthalene are to be encouraged, because they might finally provide a definitive conclusion as to whether electron transfer occurs. The issue is whether the electron transfer from aromatic to NO_2^+ is sufficiently fast to compete with C-N bond formation. That electron transfer is certainly favorable thermodynamically but it may be slow because it requires the NO_2 to distort from linearity in NO_2^+ to bent in $NO_2^{\cdot}$. Nevertheless, electron transfer is the most logical explanation for the high intramolecular selectivity that is observed despite the absence of intermolecular selectivity.

Data Availability Statement

The data underlying this study are available in the published article.

Supporting Information.

A survey of published computational results on nitration of aromatics (pdf).

Author Information

Charles L Perrin, Department of Chemistry, University of California—San Diego, La Jolla, CA 92093-0358 (*cperrin@ucsd.edu*)

Acknowledgment

The electrochemistry apparatus was purchased with the $1700 that was the author's startup fund from the UCSD Department of Chemistry.

References

1 Ingold, C. K. Structure and Mechanism in Organic Chemistry, Chapter VI, Cornell University Press: New York 1969.

2 Coombes, R.G.; Moodie, R.B.; Schofield, K. Electrophilic Aromatic Substitution. Part I. The Nitration Of Some Reactive Aromatic Compounds In Concentrated Sulphuric And Perchloric Acids. *J. Chem. Soc. B* **1968**, 800-804.
3 Moodie, R. B.; Schofield, K.; Weston, J. B. Positional selectivity in aromatic nitration occurring at the diffusion rate, *J. Chem. Soc., Chem. Commun*. **1974**, 382-383.
4 Perrin, C. L. Necessity of Electron Transfer and a Radical Pair in the Nitration of Reactive Aromatics, *J. Am. Chem. Soc.* **1977**, 99, 5516-5518.
5 Kenner, J. Oxidation and Reduction in Chemistry, *Nature* **1945**, 156, 369-370. Weiss, J. Simple electron transfer processes in systems of conjugated double bonds, *Trans. Faraday Soc*. **1946**, 42, 116-121.
6 Kurig, N.; Palkovits, R. Electrochemical nitration for organic C–N bond formation: a current view on possible N-sources, mechanisms, and technological feasibility, *Green Chem*., **2023**, 25, 7508-7517.
7 Olah, G. A.; Narang, S. C.; Olah, J. A. Nitration of naphthalene and remarks on the mechanism of electrophilic aromatic nitration, *Proc. Natl. Acad. Sci. USA*, **1981**, 78, 3298-3300.
8 Eberson, L.; Radner, F. Electron-Transfer Mechanisms in Electrophilic Aromatic Nitration, *Acc. Chem. Res*. **1987**, 20, 53-59.
9 Eberson, L.; Jönsson, L.; Radner, F. Nitration of aromatics via electron transfer; the relevancy of experiments involving generation of naphthalene radical cation in the presence of nitrogen dioxide, *Acta Chem. Scandinavica*, **197**8, B32, 749-53.
10 Eberson, L.; Radner, F. Nitration of aromatics via electron transfer. II. On the reaction between Naphthalene Radical Cation and Nitrogen Dioxide, *Acta Chem. Scandinavica*, **1980**, B34, 739-45.
11 Achord, J. M.; Hussey, C. L., Electrochemical Nitration of Aromatic Hydrocarbons in Aprotic Media, *J. Electrochem Soc*. **1981**, 128, 2556-2561.
12 Ridd, J. H. Some Unconventional Pathways in Aromatic Nitration, *Acta Chem. Scandinavica*, **1998**, 52, 11-22.
13 Ridd, J. H. The Range of Radical Processes in Nitration by Nitric Acid, *Chem. Soc. Rev*., **1991**, 20, 149-165.
14 Cardoso, S. P.; Carneiro, J. W. de M.; Nitração Aromática: Substituição Eletrofílica ou Reação com Transferência de Elétrons?, *Quim. Nova*, **2001**, 24, 381-389.
15 Morkovnik, A. S. The Oxidation-reduction Stage in the Nitration Reaction, *Russian Chem. Rev.*, **1988**, 57, 254-280.
16 Patel, S. S.; Patel, D. B.; Patel, H. D. Synthetic Protocols for Aromatic Nitration: A Review, *ChemistrySelect*, **2021**, 6, 1337-1356.
17 Olah, G. A.; Kuhn, S. J.; Flood, S. H. Aromatic Substitution. VIII. Mechanism of the Nitronium Tetrafluoroborate. Nitration of Alkylbenzenes in Tetramethylene Sulfone Solution. Remarks on Certain Aspects of Electrophilic Aromatic Substitution, *J. Am. Chem. Soc*. **1961**, 83, 4571−4580.
18 Santiago, C.; Houk, K. N.; Perrin, C. L., On "Anomalous" Selectivities in Electrophilic Aromatic Substitutions, *J. Am. Chem. Soc*. **1979**, 101, 1337-1340.
19 Olah, G. A. Mechanism of Electrophilic Aromatic Substitutions, *Acc. Chem. Res*. **1971**, 4, 240-248.
20 Olah, G. A.; Narang, S. C.; Olah, J. A.; Lammertsma, K. Recent aspects of nitration: New preparative methods and mechanistic studies (A Review), *Proc. Natl. Acad. Sci. USA*, **1982**, 79, 4487-4494.

21 Esteves, P. M., Carneiro, J. W. de M.; Cardoso, S. P.; Barbosa, A. G. H.; Laali, K. K.;| Rasul, G.; Surya Prakash, G. K.; Olah, G. A. Unified Mechanistic Concept of Electrophilic Aromatic Nitration: Convergence of Computational Results and Experimental Data, *J. Am. Chem. Soc*. **2003**, 125, 4836-4849.

22 (a) Sankararaman, S.; Haney, W. A.; Kochi, J. K. Aromatic Nitration with Ion Radical Pairs [$ArH^{\cdot+}$,$NO_2^{\cdot}$] as Reactive Intermediates. Time-Resolved Studies of Charge-Transfer Activation of Dialkoxybenzenes, *J. Am. Chem. Soc*., **1987**, 109, 5235-5249. (b) Sankararaman, S.; Kochi, J. K. Charge-transfer Nitration of Naphthalene and the Methylnaphthalenes. Part 1. Direct Comparison with Electrophilic Aromatic Nitrations, *J. Chem. Soc. Perkin Trans. 2* **1991**, 1-12.

23 Kochi, J. K. Inner-Sphere Electron Transfer in Organic Chemistry. Relevance to Electrophilic Aromatic Nitration, *Acc. Chem. Res*. **1992**, 25, 39-47.

24 Sankararaman, S.; Haney, W. A.; Kochi, J. K. Aromatic Nitration with Ion Radical Pairs [$ArH^{\cdot+}$,$NO_2^{\cdot}$] as Reactive Intermediates. Time-Resolved Studies of Charge-Transfer Activation of Dialkoxybenzenes. *J. Am. Chem. Soc*. **1987**, 109, 5235-5249.

25 Kim, E. K.; Bockman, T. M.; Kochi, J. K. The Mechanism of Charge-transfer Nitration of Naphthalene, *J. Chem. Soc. Perkin Trans. 2* **1992**, 1879-1891.

26 Kim, E. K.; Bockman, T. M.; Kochi, J. K. Electron-Transfer Mechanism for Aromatic Nitration via the Photoactivation of EDA Complexes. Direct Relationship to Electrophilic Aromatic Substitution, *J. Am. Chem. Soc*. **1993**, 115, 3091-3104.

27 (a) Kochi, J. K. Electron Transfer in the Thermal and Photochemical Activation of Electron Donor- Acceptor Complexes in Organic and Organometallic Reactions, *Adv. Phys. Org. Chem.* **1994**, 29 185-272. (b) Kochi, J. K. Electron Transfer and Charge Transfer: Twin Themes in Unifying the Mechanisms of Organic and Organometallic Reactions, *Angew. Chem. Int. Ed*. **1988**, 27, 1227-1388. (c) Bockman, T. M.; Kochi, J. K. *J. Phys. Org. Chem.* **1994**, 7, 325-351.

28 Tanaka, M.; Muro, E.; Ando, H.; Xu, Q.; Fujiwara, M.; Souma, Y.; Yamaguchi, Y. NO2+ Nitration Mechanism of Aromatic Compounds: Electrophilic vs Charge-Transfer Process, *J. Org. Chem*. **2000**, 65, 2972-2978.

29 Shopsowitz, K.; Lelj, F.; MacLachlan, M. J. Regioselectivity in the Nitration of Dialkoxybenzenes. *J. Org. Chem*. **2011**, 76, 1285-1294.

30 Pryor, W. A.; Gleicher, G. J.; Cosgrove, J. P.; Church, D. F., Reaction of Polycyclic Aromatic Hydrocarbons (PAH) with Nitrogen Dioxide in Solution. Support for an Electron-Transfer Mechanism of Aromatic Nitration Based on Correlations Using Simple Molecular Orbital Theory, *J. Org. Chem*. **1984**, 49, 5189-5194.

31 Johnston, J. F.; Ridd, J. H.; Sandall, J. P. B. The borderline between the classical and the electron transfer process in nitration by the nitronium ion. *J. Chem. Soc., Chem. Commun.* **1989**, 244-6.

32 Johnston, J. F.; Ridd, J. H.; Sandall, J. P. B. Nitrogen-15 nuclear polarization in nitration and related reactions. Part 5. The borderline between the classical and the electron-transfer mechanisms in nitration by the nitronium ion, *J. Chem. Soc. Perkin Trans. 2* **1991**, 623-8.

33 Lehnig, M. Nitration of dimethoxybenzenes, mesitylene and toluene with nitric acid and mixed acid studied by ^{15}N-CIDNP, *J. Chem. Soc., Perkin Trans. 2*, **1996**, 1943-1948.

34 (a) Koleva, G.; Galabov, B.; Hadjieva, B.; Schaefer, H. F. III; Schleyer, P. v. R., An Experimentally Established Key Intermediate in Benzene Nitration with Mixed Acid, *Angew. Chem. Int. Ed*. **2015**, 54, 14123-14127. (b) Koleva, G.; Galabov, B.; Hadjieva, B.; Schaefer,

H. F. III Corrigendum: An Experimentally Established Key Intermediate in Benzene Nitration with Mixed Acid, *Angew. Chem. Int. Ed*. **2020** *59*, 7986.

35 Galabov, B.; Nalbantova, D.; Schleyer, P. v. R.; Schaefer, H. F. III, Electrophilic Aromatic Substitution: New Insights into an Old Class of Reactions, *Acc. Chem. Res*. **2016**, 49, 1191-1199.

36 Cortona, M.; Vettorazzi, N.; Silber, J. J.; Sereno, L. Mechanistic study of the nitration of naphthalene by its electrochemical oxidation in the presence of nitrite ion in acetonitrile solution, *J. Electroanal. Chem*. **1995**, 394, 245-251.

37 (a) Cortona, M.; Vettorazzi, N.; Silber, J. J.; Sereno, L. E. Electrochemical Nitration of Naphthalene in Micellar Systems, *J. Braz. Chem. Soc.* **1997**, 8, 377-382. (b) Cortona, M.; Vettorazzi, N.; Silber, J. J.; Sereno, L. E. Electrochemical Nitration of Naphthalene in the presence of nitrite ion in aqueous non-ionic surfactant solutions, *J. Electroanal. Chem*. **1999**, 470, 157-165.

38 Boughriet, A.; Wartel, M. Mechanistic and energetic aspects of aromatic nitration with NO2+ in sulfolane, *J. Electroanal. Chem.*, **1989**, 262, 183-194.

39 Boughriet, A.; Wartel, M. Electrochemical and Thermodynamic Properties of Oxygenated Nitrogen Compounds and Aromatics in Nitromethane. Application to the Energetic Aspects of the Nitration Process via Inner-sphere and/or Outer-sphere Electron-transfer Mechanisms. *J. Chem. Soc., Chem. Commun*. **1989**, 809-810.

40 Eberson, L.; Radner, F. Nitration of polycyclic aromatic hydrocarbons by dinitrogen tetroxide. II. Synthetic and Mechanistic Aspects, *Acta Chem. Scandinavica*, **1985**, B39, 343-356.

41 Eberson, L.; Radner, F. Nitration of aromatics via electron transfer. II. On the reaction between naphthalene radical cation and nitrogen dioxide, *Acta Chem. Scand*. **1980**, B34, 739-745.

42 Boughriet, A.; Fischer, J. C.; Wartel, M.; Bremard, C. On the activation of aromatic nitration by nitrogen oxide (N_2O_4), *Nouveau J. Chim.* **1985**, 9, 651-3.

43 Eberson, L. personal communication to C. L. Perrin.

44 Gray, P.; Ioffe, A. D. The Reactivity and Structure of Nitrogen Dioxide, *Chem. Rev*. **1955**, 55, 1069-1154.