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$^{14}N/^{15}N$ Isotope Effect on the Electron Transfer Process between *N*,*N*,*N*′,*N*′-Tetramethyl-*p*-phenylenediamine and Wurster's Blue

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Appreciable $^{14}N/^{15}N$ equilibrium isotope effect has been observed for the electron-transfer process between *N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylenediamine (TMPD) and its radical cation perchlorate ($TMPD^{+\bullet}ClCO_4^-$, Wurster's blue). The equilibrium constant for the reaction, $TMPD + [^{15}N_2]TMPD^{+\bullet} \rightleftharpoons TMPD^{+\bullet} + [^{15}N_2]TMPD$, was determined to be 0.85 ± 0.05 at 25 °C in acetonitrile by electron spin resonance (ESR) analysis of the line-broadening effect of Wurster's blue in the presence of its parent neutral molecule. Redox potentials of TMPD and $[^{15}N_2]$TMPD were determined by cyclic voltammetry to be $E° = 0.107$ and 0.103 ± 0.002 V vs SCE respectively, corresponding to $K = 0.86 \pm 0.06$ for the reaction. Comparison of the infrared and Raman spectra of TMPD, $[^{15}N_2]$TMPD and their radical cations revealed significant vibrational frequency shifts caused by the heavy-atom substitution and radical cation formation, from which the free energy change for the electron-transfer process was estimated to be 300 J mol^{-1}, corresponding to $K = 0.89$. These results demonstrate that ^{15}N-substitution of TMPD decreases appreciably the ionization potential of the molecule, making it easier to lose an electron forming the corresponding radical cation in solution.

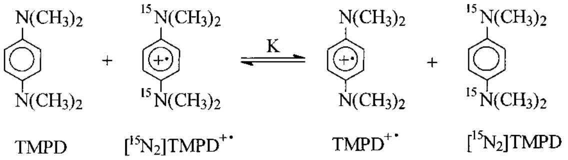
Introduction

Isotope effects and isotope enrichment have attracted much attention for a long time owing to the wide use of isotopes in a variety of scientific and technical applications. However, isotope effects in electron transfer reactions had rarely been studied until Stevenson et al. reported an unprecedented large $^{14}N/^{15}N$ equilibrium isotope effect (EIE) on the electron-transfer reaction of nitrobenzene and its radical anion in solution in 1986.[1] Then Stevenson and co-workers[2,3] published a series of papers dealing with $^1H/^2H$, $^{12}C/^{13}C$, $^{14}N/^{15}N$ and $^{17}O/^{18}O$ isotope effects on electron-transfer processes between several radical anions and their heavy isotope-substituted aromatic molecule precursors. They found that the equilibrium constants for the electron exchange reactions deviated significantly from unity and suggested that these EIEs might be used as a basis for efficient isotope separations.

However, the EIE in electron-transfer processes between radical cations and their neutral molecules had never been studied until our previous report on the significant $^1H/^2H$ EIE in the electron-transfer reaction between thianthrene and its radical cation.[4,5]

Then $^{32}S/^{33}S$, $^{12}C/^{13}C$ and $^{14}N/^{15}N$ EIEs in electron-transfer reactions between some electron-rich heteroaromatic molecules, such as thianthrene, phenothiazine, and *N*-methylphenothiazine, and their radical cations were reported from this laboratory.[6−8] Since some of the EIE is significant[6,7] and, further, radical cations and their parent molecules are quite different in chemical and physical properties, thus making them easy to separate, this finding may lead to a facile approach for isotope enrichment. Indeed, partial oxidation of a mixture of thianthrene and perdeuterated thianthrene, or phenothiazine and ^{15}*N*-phenothiazine, followed by separation of the precipitated radical cations from the neutral molecules in the solution did make the isotope distribution in the neutral molecules different from that of the original mixture.[4,7]

We report herein electron spin resonance (ESR), cyclic voltammetry (CV), infrared (IR), and Raman spectroscopic studies on $^{14}N/^{15}N$ equilibrium isotope effects on the electron-transfer reaction between *N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylenediamine (TMPD) and the radical cation of its ^{15}N-substituted analogue ($[^{15}N_2]TMPD^{+\bullet}$) in acetonitrile, eq 1:



(1)

Experimental Section

Materials. *N*,*N*,*N*′,*N*′-Tetramethyl-*p*-phenylenediamine (TMPD) was purchased from Shanghai Chemical Co. $[^{15}N_2]$TMPD was synthesized from benzene and $Na^{15}NO_3$ (99.5 atom % ^{15}N, Shanghai Institute of Chemical Engineering) by standard nitration and reduction procedures followed by methylation with dimethylsulfate, mp 49−50 °C. TMPD and $[^{15}N_2]$TMPD were purified by column chromatography on silica gel and by sublimation in a vacuum before use. The radical cation perchlorates ($TMPD^{+\bullet}ClO_4^-$ and $[^{15}N_2]TMPD^{+\bullet}ClO_4^-$) were prepared by oxidizing the corresponding parent molecule with 2,2,6,6-tetramethyl-4-acetoxypiperidine oxoammonium perchlorate in anhydrous acetonitrile by a procedure similar to that described previously,[9] mp, 138−140 °C; ESR *g* value, 2.0030.

ESR Measurements. Carefully weighed portions of $[^{15}N_2]TMPD^{+\bullet}ClO_4^-$ and TMPD were dissolved in anhydrous acetonitrile. The initial concentration of $[^{15}N_2]TMP\ D^{+\bullet}ClO_4^-$ was 3.31×10^{-4} M and the concentration ratio of TMPD/$[^{15}N_2]TMPD^{+\bullet}$ ranged from 0.41 to 4.10. The solution was placed in

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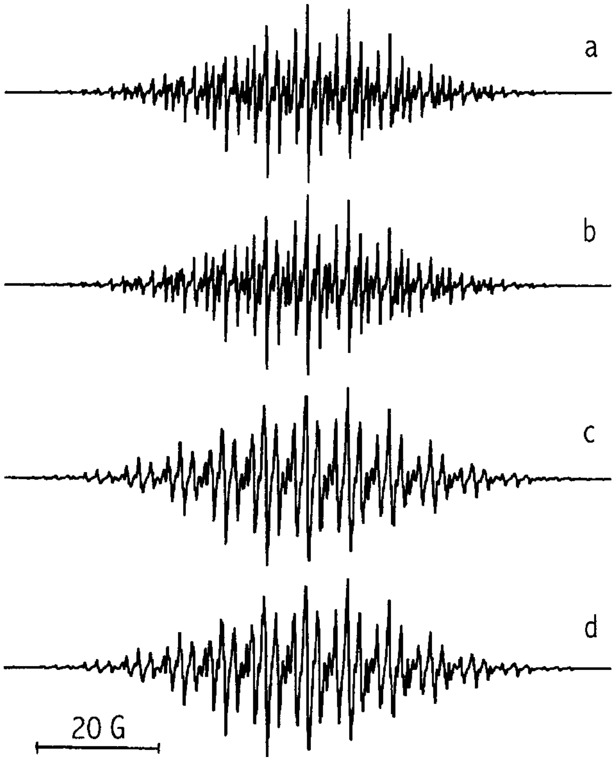

Figure 1. ESR spectra of *N*,*N*,*N′*,*N′*-tetramethyl-*p*-phenylenediamine radical cations recorded in acetonitrile solution at 25 °C. (a) $[^{15}N_2]$-TMPD$^{+\bullet}$, 3.31×10^{-4} M; (b) computer simulation of (a), line width $\Delta Hpp = 0.20$ G, for hyperfine coupling constants (hfcs) see text; (c) TMPD$^{+\bullet}$, 3.43×10^{-4} M; (d) computer simulation of (c), line width $\Delta H_{pp} = 0.20$ G, for hfcs see text.

a 2 mm glass capillary and degassed by a freeze-and thaw procedure, then sealed for ESR determinations.

ESR spectra were recorded on a Bruker ER 200D spectrometer using a standard TE_{102} rectangular cavity and operating in the X-band with 100 kHz modulation and a modulation amplitude of 0.1 G. All measurements were carried out at ambient temperature.

Spectral simulations were performed by a homemade software which is based upon the Bloch equations and rigorously accounts for the line broadening caused by electron exchange between the radical and the nonparamagnetic species in solution.[10] Hyperfine splitting constants were obtained from the spectrum of the isotopically pure radicals by computer simulation. Then the simulated spectra of the two radical cations with different isotopes were computationally superimposed with the concentration ratio as a new variable to match the experimental spectrum of the mixed radical cations. The line widths of both species were adjusted in the simulation by reference to lines that are relatively free of overlap. The equilibrium constants evaluated from the concentration ratios of the two radical cations are reproducible over several experiments with different initial concentration ratios of the radical cation/neutral molecule.

Cyclic Voltammetric Measurements. A conventional single-compartment, three-electrode cell was used for the cyclic voltammetric measurement as described previously.[11] The anhydrous acetonitrile solution containing 0.1 M $Bu_4NClO_4^-$ as the supporting electrolyte was freshly prepared, deaerated with nitrogen, and added with neutral alumina to remove residual water before each measurement. All the potentials were recorded at ambient temperature with respect to a saturated calomel electrode (SCE) reference electrode. Each experiment was repeated five times, and the standard deviation was ±2 mV.

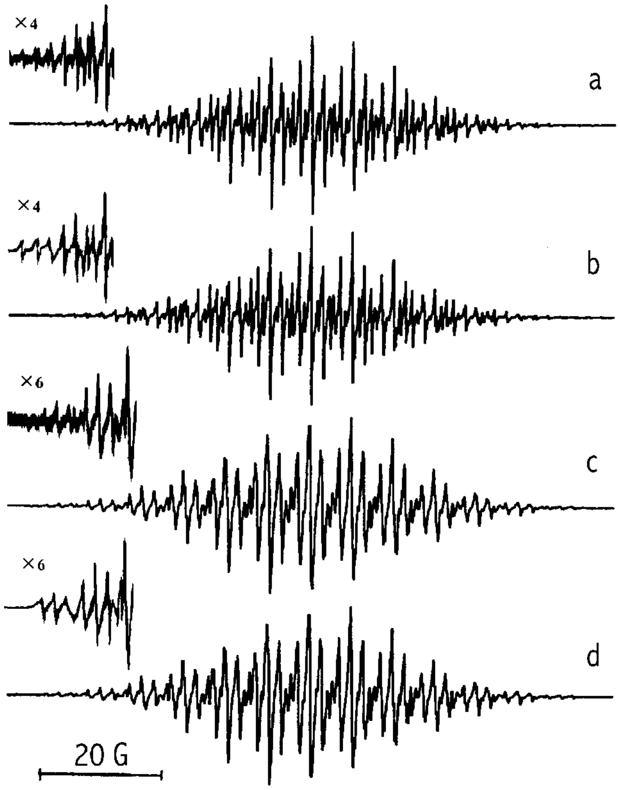

Figure 2. Representative ESR spectra obtained from a mixture of $[^{15}N_2]$-TMPD$^{+\bullet}$ and TMPD recorded in acetonitrile solution at 25 °C. (a) $[[^{15}N_2]TMPD^{+\bullet}]_0 = 3.31 \times 10^{-4}$ M, $[TMPD]_0 = 2.75 \times 10^{-4}$ M; (b) computer simulation of (a) generated by using a molar ratio of $[^{15}N_2]$-TMPD$^{+\bullet}$/TMPD$^{+\bullet}$of 1:0.77, corresponding to $K = 0.86$ for reaction 1; (c) $[[^{15}N_2]TMPD^{+\bullet}]_0 = 3.31 \times 10^{-4}$ M, $[TMPD]_0 = 1.37 \times 10^{-3}$ M; (d) computer simulation of (c) generated by using a molar ratio of $[^{15}N_2]$-TMPD$^{+\bullet}$/TMPD$^{+\bullet}$of 1:3.57, corresponding to $K = 0.83$ for reaction 1.

IR and Raman Spectroscopy Measurements. IR spectra were recorded on a Nicolet 170 SX IR spectrometer using KBr pellets. Raman spectra were recorded on a Spex 1403 laser Raman spectrometer with an argon-ion laser excitation at 514.5 nm at room temperature using KBr pellets.

Results

A. ESR Spectroscopic Studies. Wurster's blue (TMPD$^{+\bullet}$-ClO_4^-) showed well-resolved ESR spectrum in dilute anhydrous acetonitrile solution at room temperature (Figure 1c) that are characterized by a triplet of the ^{14}N hyperfine splitting of 7.082 G and proton splittings from the methyl (6.815 G, 12H) and aromatic (1.980 G, 4H) protons, which are in good accordance with those reported in the literature.[12] The ESR spectrum of $[^{15}N_2]TMPD^{+\bullet}ClO_4^-$ was reported for the first time, which is characterized by a doublet of ^{15}N splitting of 9.915 G and proton splittings which are the same as those in $TMPD^{+\bullet}ClO_4^-$ (6.815 G, 12H, and 1.980 G, 4H) (Figure 1a). Addition of neutral TMPD to the acetonitrile solution of $[^{15}N_2]TMPD^{+\bullet}ClO_4^-$ resulted in a change of the ESR spectrum from the unique $[^{15}N_2]TMPD^{+\bullet}ClO_4^-$ spectrum to a superimposed spectrum of $[^{15}N_2]TMPD^{+\bullet}ClO_4^-$ and $TMPD^{+\bullet}ClO_4^-$, accompanied by appreciable line broadening, as illustrated in Figure 2. This demonstrates unambiguously the occurrence of the electron transfer between $[^{15}N_2]TMPD^{+\bullet}$and TMPD as depicted in eq 1. Computer simulation of the ESR spectra from eight independent experiments with an initial concentration ratio of TMPD/$[^{15}N_2]TMPD^{+\bullet}$ranging from 0.41 to 4.10 gave an equilibrium constant $K = 0.85 \pm 0.05$ at 25 °C in acetonitrile for

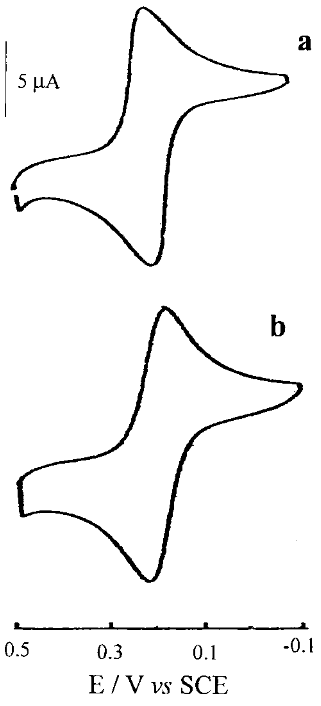

Figure 3. (a) Cyclic voltammograms of TMPD and (b) [$^{15}N_2$]TMPD recorded at a glassy carbon electrode in acetonitrile solutions at 25 °C. Potentials were recorded vs SCE.

reaction 1. Details of the simulation procedure have been reported previously.[8]

B. Cyclic Voltammetric Studies. TMPD and [$^{15}N_2$]TMPD in acetonitrile solution showed nice reversible cyclic voltammograms (Figure 3). Thus, the standard potential for the redox couple TMPD/TMPD$^{+\bullet}$may be obtained according to Nernst equation:[13]

$$E^{\circ}_{\mathrm{Ox/Red}} = \frac{E_{\mathrm{pa}} + E_{\mathrm{pc}}}{2} + \frac{0.029}{2}\,\mathrm{lg}\,\frac{D_{\mathrm{Ox}}}{D_{\mathrm{Red}}} \tag{2}$$

where $E^{\circ}_{\mathrm{Ox/Red}}$ is the standard electrode potential, E_{pa} and E_{pc} are the anodic and cathodic peak potentials respectively, and D_{Ox} and D_{Red} are the diffusion coefficients of oxidation and reduction state, respectively. In reversible processes, the ratio of $D_{\mathrm{Ox}}/D_{\mathrm{Red}}$ is close to unity; hence, the standard electrode potential may be expressed as

$$E^{\circ}_{\mathrm{Ox/Red}} = \frac{E_{\mathrm{pa}} + \mathrm{E}_{\mathrm{pc}}}{2} \tag{3}$$

Standard electrode potentials for the redox couples of TMPD$^{+\bullet}$/TMPD and [$^{15}N_2$]TMPD$^{+\bullet}$/[$^{15}N_2$]TMPD were determined to be 0.107 ± 0.002 V and 0.103 ± 0.002 V vs SCE, respectively, from five independent measurements. Obviously, ^{15}N-substitution makes TMPD lower its ionization potential. The equilibrium constant for reaction 1 can be easily calculated from eqs 4 and 5 as 0.86 ± 0.06, which is in good consistent with the ESR result mentioned above.

$$K = \exp(-\Delta G^{\circ}/RT) \tag{4}$$

$$\Delta G^{\circ} = -\mathrm{F}\,(E^{*\circ} - E^{\circ}) \tag{5}$$

where E° and $E^{*\circ}$ represent the standard electrode potentials of the light- and heavy-isotope substituted redox couples, respectively.

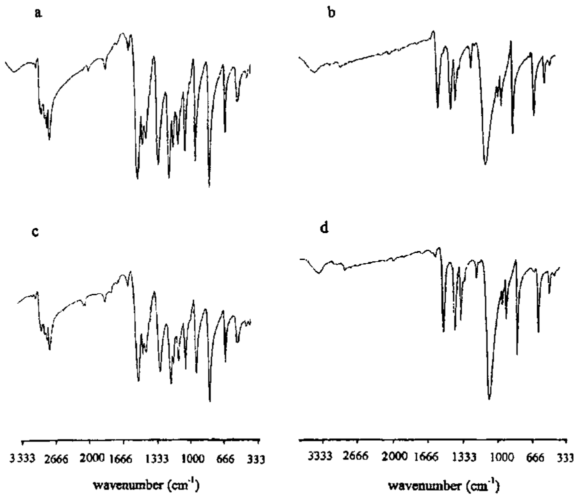

Figure 4. (a) IR spectra of TMPD, (b) TMPD$^{+\bullet}$, (c) [$^{15}N_2$]TMPD, (d) [$^{15}N_2$]TMPD$^{+\bullet}$.

C. IR and Raman Studies. We have found that significant frequency shifts took place in some of the IR and Raman bands of thianthrene, phenothiazine, and *N*-methylphenothiazine upon the heavy-atom substitution and radical cation formation, which may explain the isotope effect.[5−8] Therefore, IR and Raman spectra of TMPD, [$^{15}N_2$]TMPD and their radical cation perchlorates were recorded. The IR spectra of TMPD, [$^{15}N_2$]TMPD, TMPD$^{+\bullet}$ClO$_4^-$, and [$^{15}N_2$]TMPD$^{+\bullet}$ClO$_4^-$ are shown in Figure 4. The Raman spectra are in consistent with those reported in the literature.[14,15]

TMPD, [$^{15}N_2$]TMPD and their radical cations with 28 atoms and D_{2h} symmetry have 78 fundamental vibrations. According to the D_{2h} point group the 78 fundamental vibrations can be classified as $13A_g + 12B_{1g} + 8B_{2g} + 6B_{3g} + 7A_u + 8B_{1u} + 12B_{2u} + 12B_{3u}$. The IR and Raman spectral assignments of TMPD have been reported previously.[14,16] The IR spectral assignment of TMPD radical cation was performed by using the similar procedure and with reference to its Raman spectral assignment.[14,15] The assignment of the ^{15}N-substituted species are straightforward since they showed similar IR and Raman spectra to those of their ^{14}N analogue and some low-frequency shifts are obvious due to the heavy isotope substitution. The complete IR and Raman spectral assignments are listed in Tables 1 and 2.

It can be seen from Tables 1 and 2 that replacement of ^{14}N atoms by ^{15}N and transformation of TMPD and [$^{15}N_2$]TMPD to their radical cations bring about significant frequency shifts of, not only the C−N stretching, but also some of C−C and C−H vibrations in the phenyl ring. Therefore, isotopic substitution and radical cation formation should result in a nonzero enthalpy change for reaction 1. For instance, taking into account of the B_{3u} N−Ph antisymmetric stretching band of TMPD at 1322 cm^{-1} only, which is shifted to 1308 cm^{-1} by the ^{15}N-substitution, and to 1341 cm^{-1} by the radical cation formation, the enthalpy of reaction 1 would increase 107.9 J mol^{-1}. Vibrational bands that are effective for the enthalpy change of reaction 1 are summarized in Table 3. The remaining vibrations showed very small effects and are not included in the table. On the basis of these vibrations the enthalpy change due to the zero-point energy effect of reaction 1 can be estimated as 300 J/mol. Since electron transfer between two structurally similar species would not bring about an entropy change,[17] hence giving an identical free energy and enthalpy change, the equilibrium constant of reaction 1 can be estimated to be 0.89, in accordance with the ESR and cyclic voltammetric results given above.

TABLE 1: Fundamental Vibrational Frequencies (cm^{-1}) of IR Spectra for TMPD, TMPD$^{+\bullet}$, [^{15}N$_2$]TMPD, and [^{15}N$_2$]TMPD$^{+\bullet a}$

TMPD	TMPD$^{+\bullet}$		[^{15}N$_2$]TMPD		[^{15}N$_2$]TMPD$^{+\bullet}$	assignments
2941(m)	2945	2942(m)	2950	2930(m)	2935(m)	CH$_3$ deg str (B$_{1u}$,B$_{2u}$,B$_{3u}$)
2871(m)	2873	2871(m)	2873			CH$_3$ deg str (B$_{1u}$,B$_{2u}$,B$_{3u}$)
2828(m)	2829	2824(m)				CH$_3$ sym str (B$_{2u}$,B$_{3u}$)
2780(m)	2786	2782(s)				CH$_3$ sym str (B$_{2u}$,B$_{3u}$)
1473(s)	1476	1472(s)	1474	1421(vs)	1421(vs)	CH$_3$ deg def (B$_{1u}$,B$_{2u}$,B$_{3u}$)
1442(s)	1445	1442(s)	1445	1378(vs)	1369(vs)	CH$_3$ deg def (B$_{1u}$,B$_{2u}$,B$_{3u}$)
	1407		1405			CH$_3$ sym def (B$_{2u}$,B$_{3u}$)
1128(vs)	1131	1124(s)	1127	1092(vs)	1092(vs)	CH$_3$ deg rock (B$_{1u}$,B$_{2u}$,B$_{3u}$)
1056(vs)	1058	1059(vs)	1055	1092(vs)	1092(vs)	CH$_3$ deg rock (B$_{1u}$,B$_{2u}$,B$_{3u}$)
	3063		3062			CH str (B$_{3u}$)
3047(m)		3047(m)		3049(w)	3080(w)	CH str (B$_{3u}$)
1614(s)	1521	1614(s)	1520	1611(w)	1610(m)	ring def (B$_{3u}$)
1521(vs)		1519(vs)		1541(vs)	1530(vs)	ring def (B$_{3u}$)
1175(s)	1178	1175(s)	1178	1193(w)	1194(w)	CH ip bend (B$_{2u}$)
1001(m)	1002	1001(m)	1002	973(s)	974(s)	star of David vibration (B$_{3u}$)
812(vs)	814	812(vs)	813	826(vs)	826(vs)	CH op bend (B$_{1u}$)
531(vs)		527(vs)		516(s)	516(s)	ring op def (B$_{1u}$)
	535		530			ring op def (B$_{1u}$)
1322(vs)	1325	1308(vs)	1310	1341(m)	1336(m)	N−Ph antisym str (B$_{3u}$)
1215(vs)	1216	1202(vs)	1204	1230(s)	1221(s)	N−(CH$_3$)$_2$, antisym str (B$_{3u}$)
951(vs)	953	944(vs)	946	940(s)	934(s)	N−(CH$_3$)$_2$, sym str (B$_{2u}$)
655(vs)	657	651(vs)	643	621(vs)	622(vs)	NC2, scissors (B$_{3u}$)
445(m)	449	442(m)		462(m)	462(m)	NC2, wag (B$_{1u}$)
409(m)		409(m)		432(w)	432(w)	NC2, rock (B$_{2u}$)

[a] def = deform, deg = degenerate, str = stretching, ip = in-plane, op = out-of-plane, sym = symmetric, antisym = antisymmetric.

TABLE 2: Fundamental Vibrational Frequencies (cm^{-1}) of Raman Spectra for TMPD, TMPD$^{+\bullet}$, [^{15}N$_2$]TMPD, and [^{15}N$_2$]TMPD$^{+\bullet a}$

TMPD	TMPD$^{+\bullet}$	[^{15}N$_2$]TMPD	[^{15}N$_2$]TMPD$^{+\bullet}$	assignments
1477	1477			CH$_3$ deg (A$_g$,B$_{1g}$,B$_{2g}$,B$_{3g}$)
1442	1442			CH$_3$ deg (A$_g$,B$_{1g}$,B$_{2g}$,B$_{3g}$)
1409	1409	1417	1412	CH$_3$ sym def (A$_g$,B$_{1g}$)
1137	1137			CH$_3$ deg rock (A$_g$,B$_{1g}$,B$_{2g}$,B$_{3g}$)
1621	1621	1629	1627	ring str (A$_g$)
1562	1562			ring str (B$_{1g}$)
1314	1307			CH ip bend (A$_{1g}$)
1204	1204	1223	1223	CH ip bend (A$_g$)
778	768	767	766	ring breathing (A$_g$)
715	715			ring op def (B$_{2g}$)
642	642			ring ip def (B$_{1g}$)
492	493			ring ip def (A$_g$)
1340	1327	1504	1504	N−Ph sym str (A$_g$)
1153	1153	1168	1168	N−(CH$_3$)$_2$, antisym str (B$_{1g}$)
940	939	928	925	N−(CH$_3$)$_2$, sym str (A$_g$)
512	512	513	514	NC2 scissors (A$_g$)
312	312	325	322	NC2 rock (B$_{1g}$)
270	266			N−Ph ip bend (B$_{1g}$)
174	172			NC2, twist (B$_{3g}$)

[a] def = deform, deg = degenerate, str = stretching, ip = in-plane, op = out-of-plane, sym = symmetric, antisym = antisymmetric.

TABLE 3: Selected IR and Raman Frequencies (cm^{-1}) of TMPD, TMPD$^{+\bullet}$, [^{15}N$_2$]TMPD, and [^{15}N$_2$]TMPD$^{+\bullet}$ That Contribute to $\Delta H°$ for Reaction 1^a

assignments^b	TMPD	TMPD$^{+\bullet}$	[^{15}N$_2$]TMPD	[^{15}N$_2$]TMPD$^{+\bullet}$	contribution to $\Delta H°$ (J/ mol)
B$_{3u}$ C−C ring def	1521	1541	1519	1530	−107.9
B$_{1u}$, B$_{2u}$, B$_{3u}$ CH$_3$ deg def	1442	1378	1442	1369	−107.9
B$_{3u}$ N−ph antisym str	1322	1341	1308	1336	107.9
B$_{3u}$ N−(CH$_3$)$_2$ antisym str	1215	1230	1202	1221	48.1
B$_{1u}$, B$_{2u}$, B$_{3u}$ CH$_3$ deg rock	1122	1092	1124	1092	48.1
B$_{3u}$ NC$_2$ scissors	655	621	651	622	59.8
B$_{1u}$ ring op def	531	516	527	516	48.1
A$_g$, B$_{1g}$ CH$_3$ sym def	1400	1417	1409	1412	−59.8
A$_g$ N−Ph sym str	1340	1504	1327	1504	115.6
A$_g$ ring breathing	778	767	768	766	−107.9

[a] Total contribution to $\Delta H°$ = 300 J /mol. [b] def = deform, deg = degenerate, str = stretching, op = out-of-plane, sym = symmetric, antisym = antisymmetric.

Discussion

The concordant experimental results mentioned above demonstrate clearly that the electron transfer from TMPD to its ^{15}N-substituted radical cation is isotopically selective. Electron transfers preferentially from the heavy-isotope substituted molecule ([^{15}N$_2$]TMPD) to its light-isotope substituted radical cation (TMPD$^{+\bullet}$). In other words, it is easier for the neutral heavy-isotope substituted molecule to lose an electron than it is for the light-isotope substituted molecule to form the corresponding radical cation, and ^{15}N-substitution appreciably decreases the ionization potential of the neutral TMPD and the electron affinity of its radical cation. Similar ^{15}N/^{14}N equilibrium isotope effect has been observed in nitrobenzene/nitrobenzene radical anion system when the counterion was sodium ion where [^{15}N]nitrobenzene possesses a lower electron affinity for solvated electrons in liquid ammonia than [^{14}N]nitrobenzene.[1,18] ^{15}N-Substituted phenothiazine also possesses lower ionization potential than its ^{14}N-analogue.[7] It is seen from Table 3 that the N−Ph symmetric and unsymmetric stretching frequencies of TMPD and [$^{15}N_2$]TMPD are most remarkably increased upon forming the corresponding radical cations, and the change is more pronounced for [$^{15}N_2$]TMPD. This suggests that the N−Ph bonds in the radical cations are significantly strengthened and possessing partial double bond character, and ^{15}N-substitution makes this change more pronounced. In addition, the C−C ring deform frequencies are increased while the ring rock and breathing frequencies are decreased upon radical cation formation, suggesting a partial destruction of the aromatic ring structure and formation of a quinone-like structure, but ^{15}N-substitution makes these changes less pronounced. Therefore, the overall effect is making the enthalpy change of reaction 1 positive and the equilibrium constant of reaction 1 less than unity.

In conclusion, this work demonstrates that electron transfers in an isotopically selective manner between TMPD and its radical cation in solution. The ^{15}N-substitution decreases the ionization potential of TMPD and the electron affinity of its radical cation. This equilibrium isotope effect can be rationalized by zero-point energy difference caused by the heavy isotope substitution.

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