

Supporting Information for:

Estimation of Self-Exchange Electron Transfer Rate Constants for Organic Compounds from Stopped-Flow Studies

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Preparation of $iPr_2N)_2-d_6$. The same method was used as for $iPr_2N)_2$ except that acetone- d_6 was used instead of acetone for the reductive alkylation of 1,1-diisopropylhydrazine. The NH hydrogens of 1,1-diisopropyl hydrazine were exchanged for deuterium before the reduction, which proved to be necessary to avoid extensive loss of deuterium at the methyl hydrogens during this reaction. The isotopic enrichment of the sample obtained was found by mass spectroscopy to be $d_6 : d_5 : d_4 = 67.3 : 11.7 : 1.4$, confirmed using several scans, each giving the same ratios. From these ratios the actual enrichment is 97% d_6 , that is, our sample is $iPr_2N)_2-d_{5.82}$.

ET rate determination for $iPr_2N)_2^{0/+}$ by 2H NMR. $iPr_2N)_2-d_6$ was sublimed in a sealed glass tube (at 0.5 mm Hg). The radical cation nitrate $iPr_2N)_2[NO_3]^+$ was recrystallized twice by vapor diffusion of ether into an acetonitrile solution, and large, well formed crystals were selected. In a typical experiment hydrazine- d_6 (7.19 mg, 0.0348 mmol) was dissolved in a 602 μ L aliquot of a CH_3CN/CD_3CN mixture prepared by diluting 87 μ L of CD_3CN with CH_3CN in a 25 mL volumetric flask (CD_3CN is present because its 2H signal is used to check the stability of the instrument). A spectrum of the hydrazine sample was taken after shimming on the FID and optimization of all the experimental parameters. The sample was removed from the probe, tilted, uncapped, and the crystals of the radical cation (9.08 mg, 0.0346 mmol) were placed inside on

the side of the tube. The cap was replaced, the time recorded and the crystals shaken down into the solution. The average of this time and the time when the crystals dissolved (about 30 seconds) was considered to be the initial time T_0 . The tube was placed back into the probe and a spectrum was taken. For every spectrum the T_{start} time was recorded, and it takes very close to $T_c = AQ \times NS$ to collect a spectrum. The time used in further calculations is $t = ([T_s + T_c]/2) - T_0$ s. Spectra were taken every 10 minutes. Concentrations were calculated using 618 μL as the volume of the solutions. Lorentzian line-broadening was applied (it was found that $LB = 1$ Hz gives the most consistent results) and the spectra were Fourier-transformed. The second spectrum was carefully phased and all the other spectra were phased using the PK command. The second spectrum was carefully integrated (20 Hz to -25 Hz for CD_3CN and -50 Hz to -100 Hz for the hydrazine signal) 4 times selecting a new baseline every time. The average intensity was taken. All other spectra were integrated selecting starting points for the baseline and the integrals from the same region as in the second spectrum. It was found that the phase and absolute intensity are different in the first spectrum (before addition of radical cation), making it a useless "starting point". The intensities thus obtained were used to obtain the concentration vs time dependence that was used in the subsequent fits to obtain the rate constant. The first step is to set the normalized intensity in the initial spectrum to the initial concentration $[D^0]_0$ and then normalize all the other data to that. This first point is anomalous on the graph of $[D^0]_t$ vs. t , believed to be due to "dilution" upon the addition of the radical cation (the volume increases by a few percent) and to different line shapes caused by faster spin-lattice relaxation in the presence of the radical cation, which affects integration. Using **D** and **H** to designate the labeled and unlabeled material, and a superscript to show the charge present, and subscript 0 to indicate the initial concentrations,

if $\lambda = [\text{H}^+]_0 / [\text{D}^0]_0$, Equation 5 gives the relationship between $[\text{D}^0]$ and time as a function of the rate constant k used for determining k by non-linear least squares fit:

$$[\text{D}^0] = \{[\text{D}^0]_0 \lambda \exp[-(\lambda+1) k [\text{D}^0]_0 t] + [\text{D}^0]_0\} / (\lambda + 1) \quad (5)$$

We used the $[\text{D}_0]$ values with Eq. 5 as a first estimate, k_1 , of the rate constant. From k_1 we calculate the concentration $[\text{D}^0]$ at the second point and re-normalize the data using that point, and another regression run gives a second estimate of the rate constant, k_2 . This process was continued until convergence is achieved (value of k_2 after regression is the same as that used to normalize the data before regression). Other points can be chosen for the process, and if the data are good, the k obtained does not depend upon which point is chosen. The probe was set at 298 K, and the temperature independently measured using a methanol thermometer based on the chemical shift difference, using $T(^{\circ}\text{C}) = 129.84 - 29.46 \Delta\delta - 66.2 (0.6 \Delta\delta)^2$.¹⁷ An ethylene glycol thermometer gave a temperature of 24.3°C for the 25.9°C methanol thermometer runs, and similar temperature differences between the two were observed at other temperatures. It is not clear that use of chemical thermometers gives better temperatures than the spectrometer's thermocouple.

ET rate determination for $\text{iPr}_2\text{N}_2^{\text{O}+}$ by ^1H NMR. The principal differences in this experiment from the ^2H experiment are that CD_3CN was used as solvent, and an AC-250 spectrometer was used instead of the AM-500. It is very important to avoid saturation of the signal, and its intensity increases over the course of the reaction. Shimming is easier in this case since the lock signal is available. The signal-to-noise ratio is not as much of a problem with even less scans, allowing for more data points. (23 were obtained over an 8000 s period vs. only 15 for ^2H NMR experiments). LB = 0.2 Hz was applied to the data. Subsequent integration gave the intensities.

The intensity of the standard did not change over the course of the experiment and no normalization was used. Although the change in intensity in this case is smaller (3/24) than in the case of ^2H NMR (1/2), ^1H NMR is about 50 times more sensitive than ^2H NMR, and the ^1H NMR experiment gives better data, both in terms of the number of points obtained and their scatter relative to Eq. 4. The total number of hydrogen atoms on the four isopropyl groups of the sample used is $18.18 = (24.00 - 5.82)$, and the expression for converting the raw intensities into $[\text{D}^0]$ is given in Equation 6:

$$[\text{D}^0] = [\text{D}^0]_0 / 5.82 [24.00 - 18.18 I(t)/I(t_0)] \quad (6)$$

Crystal structures. Crystal sizes: $\text{iPr}_2\text{N})_2$ $0.6 \times 0.4 \times 0.4$ mm, $\text{cHx}_2\text{N})_2$ $0.45 \times 0.3 \times 0.3$ mm, $\text{k33})_2\text{PD}^+\text{PF}_6^-$ $0.5 \times 0.25 \times 0.2$ mm, $\text{k33N})_2$ $0.4 \times 0.3 \times 0.4$ mm. Intensity data were measured with a Siemens P4/CCD diffractometer using graphite monochromated $\text{MoK}\alpha$ radiation ($\lambda = 0.71073$ Å) at 133(2) K for the first three structures, and with a Siemens P4 diffractometer using graphite monochromated $\text{Cu K}\alpha$ radiation ($\lambda = 1.54178$ Å) at 113 K for $\text{k33N})_2$. The structures were solved using the SHELXS-86 program^{18a} and refined using the SHELXS-93 program^{18b} which refines on F^2 values. Table 7 summarizes the crystal data and refinement.

References

17. van Geet, A. L.; *Anal. Chem.* **1970**, *42*, 679.
18. (a) Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467. (b) Sheldrick, G. M. *J. Appl. Crystallogr.* In preparation.

Table 7. Summary of crystal data and refinement parameters

compound	iPr₂N) ₂	cHx₂N) ₂	k33N) ₂ PD	k33N) ₂
formula	C ₁₂ H ₂₈ N ₂	C ₂₄ H ₄₄ N ₂	C ₂₂ H ₂₈ F ₆ N ₂ O ₂ P	C ₁₆ H ₂₄ N ₂ O ₂
cryst. system	monoclinic	monoclinic	monoclinic	monoclinic
space group	C2/c	P2 ₁ /n	P2 ₁ /c	P2 ₁ /n
a, Å	15.6599(4)	14.1857(3)	6.6868(3)	6.570(2)
b, Å	8.1013(2)	11.7741(2)	12.3889(4)	9.4254(6)
c, Å	11.8231(3)	14.3771(2)	13.3803(5)	11.546(2)
β, deg.	113.919(2)	111.615(2)	96.863(2)	96.17(2)
vol, Å ³	1370.25(6)	2232.46(7)	1100.51(7)	710.8(2)
Z	4	4	2	2
density ^a	0.971	1.073	1.501	1.291
F(000)	456	808	518	300
R,R _w (obsd),%	8.16/16.44	14.66/37.37	6.44/13.92	4.31/11.07
R,R _w (all),%	9.73/17.78	15.67/38.18	7.21/14.63	4.43/11.22
gof ^b	1.091	1.170	1.179	1.038

a. Calculated, Mg/m³. b. Goodness of fit.