J|A|C|S
A R T I C L E S

Inductive vs Solvation Effects in Primary Alkyl Amines: Determination of the Standard Potentials

José Luis Bourdelande, Iluminada Gallardo,* and Gonzalo Guirado*

Contribution from the Departament de Química, Universitat Autònoma de Barcelona, E-08193 Bellaterra, Barcelona, Spain

Received August 12, 2006; Revised Manuscript Received October 27, 2006; E-mail: Iluminada.Gallardo@uab.es; Gonzalo.Guirado@uab.es

---

Abstract: The determination of the standard potential of alkyl primary amines is reported for the first time using the nanosecond equilibrium method. The versatility and accuracy of the method demonstrates that it is not only an alternative to the classical and modern electrochemical methods, but also a powerful tool for quantifying inductive and/or solvation effects in a related family of compounds. Two different trends were observed depending on alkyl chain length. For "short-chain" alkyl primary amines, where the solvation around the amino group is expected to be the same, the standard potential value appears to follow a linear relationship with the number of carbon atoms, which indicates that the methylene group ($-CH_2-$) causes an inductive effect that is responsible for the stabilization of the amine cation radical. Meanwhile, the $E°$ rises slightly to a constant potential value 1.500 V for "long-chain" unbranched alkyl primary amines. This interesting result can be explained by a steric inhibition of solvation around the amino group due to a fold of the long alkyl chain following a solvent exclusion mechanism.

---

1. Introduction

The accurate standard potential ($E°$) determination of organic molecules is fundamental for the understanding of innumerable chemical and biological electron-transfer reactions.[1] Cyclic voltammetry using ultramicroelectrodes is probably the most widely used method for the direct determination of $E°$ values when fast follow-up chemical reactions are coupled to electron transfer.[2] The experimental error found in those electrochemical determinations is around 0.2 kcal mol^{-1} for electrochemically irreversible couples, which is adequate for most of the processes studied. Other methods based on pulse radiolysis,[3] and recently theoretical[4] (quantum chemical) predictions, have also been developed to obtain those $E°$ values. In this sense, in some cases an extremely accurate method for the determination of $E°$ would be highly desirable as it would make it possible to relate them to bond dissociation energies, pK_a's, inductive and/or solvation effects.[5−6] This problem can be successfully addressed using the nanosecond equilibrium method,[5] in which the measure of equilibrium constants close to 1 makes it possible to accurately determine the thermodynamically meaningful standard potential of unstable radical cations.

The propensity of alkyl primary amine cation radicals for being attached to the electrode surfaces after an EC mechanism (E: electrochemical reaction, C: chemical reaction) does not make it possible to establish their $E°$ values electrochemically.[7] Hence, the aim of this work is to determine the $E°$ values for those alkylamines using the nanosecond equilibrium method, showing that it is not only an alternative to the classical and modern electrochemical techniques but also a powerful tool for quantifying inductive and/or solvation effects in a related family of compounds.

2. Results and Discussion

2.1. Experimental Approach to the Nanosecond Equilibrium Method. Transient absorption spectroscopy using nanosecond-pulse laser excitation (nanosecond laser flash) represents an ideal technique for performing these experiments. The photooxidant system, which is based on photoinduced electron transfer, was selected to set up the electron-transfer equilibrium experiments, taking into account several previously described criteria.[5,8] This is summarized in Scheme 1 for a positive charge electron acceptor, A^+ (*N*-methylquinolinium cation), solutions (OD ≈ 0.5 at 355 nm) containing 1 M toluene were prepared in anhydrous acetonitrile. Irradiation of A^+ at 355 nm generates its singlet excited state, A^{+*}, which is a powerful one-electron oxidant ($E° = 2.7$ V vs SCE). Thus, A^{+*} reacts with toluene (C), which is used as a cosensitizer ($E° = 2.35$ V vs SCE) via exothermic electron transfer (k_{et}) to generate the geminate

---

(1) Balzani, V., Ed. *Electron Transfer in Chemistry*; J. Wiley and Sons: U.K., 2001.

(2) (a) Wightman, R. M.; Wipf, D. O. *Electroanal. Chem.* **1989**, *15*, 267. (b) Andrieux, C. P.; Hapiot, P.; Saveant, J.-M. *Chem. Rev.* **1990**, *90*, 723. (c) Amatore, C.; Bouret, Y.; Maisonhaute, E.; Abruna, H. D.; Goldsmith, J. I. *C. R. Chim.* **2003**, *6*, 99.

(3) For reviews, see: (a) Wardman, P. *J. Phys. Chem. Ref. Data* **1989**, *18*, 1637. (b) Stanbury, D. M. In *General Aspects of the Chemistry of Radicals*; Alfassi, Z. B., Ed.; Wiley: New York, 1999; Chapter 11.

(4) Fu, Y.; Liu, L.; Yu, H.-Z.; Wang, Y.-M.; Guo, Q.-X. *J. Am. Chem. Soc.* **2005**, *127*, 7227.

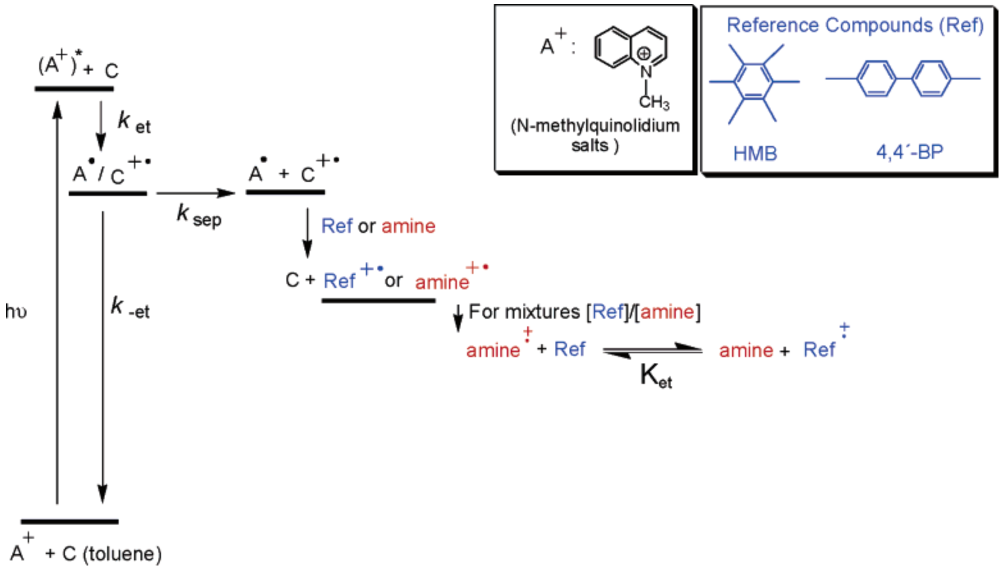
(5) (a) Guirado, G.; Fleming, C. N.; Lingenfelter, T. G.; Williams, M. L.; Zuilhof, H.; Dinnocenzo, J. P. *J. Am. Chem. Soc.* **2004**, *126*, 14086.

(6) See, for example: (a) Wayner, D. D. M.; Parker, V. D. *Acc. Chem. Res.* **1993**, *26*, 287. (b) Maslak, P.; Vallombroso, T. M.; Chapman, W. H., Jr.; Narvaez, J. N. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 73.

(7) (a) Mann, C. K.; Barnes, K. K. *Electrochemical Reactions in Nonaqueous Systems*; Marcel Dekker: New York, 1970. (b) Portis, L. C.; Bhat, V. V.; Mann, C. K. *J. Org. Chem.* **1970**, *35*, 2175. (c) Adenier, A.; Chehimi, M. M.; Gallardo, I.; Pinson, J.; Vila, N. *Langmuir* **2004**, *20*, 8243.

10.1021/ja0656245 CCC: $37.00

Scheme 1. Energy Diagram for Photoinduced Electron Transfer



radical/radical cation pair $A^{\bullet}/C^{+\bullet}$. The oxidation potential of the cosensitizer is chosen in order for diffusional separation (k_{sep}) to compete effectively with return electron transfer (k_{-et}), resulting in a high yield of separated ion radicals. Note that in this case separation of the $A^{\bullet}C^{+\bullet}$ pair will be efficient even in moderate polar solvents due to the absence of the electrostastic barrier that characterizes the diffusional separation of anion/cation radical pairs. The separated $C^{+\bullet}$ then oxidizes either the reference compound (Ref) or the amine to generate the corresponding cation radical.[9] Note that all the previous $E°$ determinations reported by using the current method were performed when the reference and substrate radical cation showed a UV−vis spectrum.[5]

For these experiments, hexamethylbenzene (HMB) was chosen as a reference compound ($E° = 1.580$ V and vs SCE),[10] since the differences in standard potential of the Ref−amine pair should be smaller than 0.1 V (eq 1).[11] The oxidation of HMB gives rise to a stable radical cation that absorbs between 400 and 540 nm, whereas the alkyl amine cation radical is transparent in this selected wavelength window. Irradiation of [HMB]/[amine] mixtures affords a mixture of the corresponding cation radicals, which are in equilibrium with the neutral compounds. On the other hand, this equilibrium takes place for a period of time of a few nanoseconds (60−120 ns). After this equilibrium time the components of the equilibrium evolve to oxidation products. We need to monitor the absorption spectrum of the HMB cation radical in such a short time scale.

$$\mathrm{amine}^{+\bullet} + \mathrm{Ref} \overset{K_{et}}{\rightleftharpoons} \mathrm{amine} + \mathrm{Ref}^{+\bullet} \qquad K_{et} = \frac{[\mathrm{amine}]\,[\mathrm{Ref}^{+\bullet}]}{[\mathrm{amine}^{+\bullet}]\,[\mathrm{Ref}]} \tag{1}$$

$$A_{measured,i} = A_{Ref,i}\left(\frac{K_{et}[\mathrm{Ref}]}{([\mathrm{amine}] + K_{et}[\mathrm{Ref}])}\right) + A_{amine,i}\left(\frac{[\mathrm{amine}]}{([\mathrm{amine}] + K_{et}[\mathrm{Ref}])}\right) \tag{2}$$

$$A_{measured,i} = A_{Ref,i}\left(\frac{K_{et}[\mathrm{Ref}]}{([\mathrm{amine}] + K_{et}[\mathrm{Ref}])}\right) + B_{amine}\ ;\ A_{amine,i} = B_{amine} \approx 0 \tag{3}$$

$$E° = E°(\mathrm{Ref}^{+\bullet}/\mathrm{Ref}) - E°(\mathrm{amine}^{+\bullet}/\mathrm{amine}) = -(RT/F)\ln K_{et} \tag{4}$$

Thus, the corresponding equilibrium constant was determined by fitting the measured spectra in different [Ref]/[amine] relative concentrations at wavelength i, $A_{measured,i}$, with the simulated ones obtained by combining the spectra of "pure" cation radicals, $A_{Ref,i}$ and $A_{amine,i}$, at wavelength i (eq 2).[12,13] In the case of alkyl primary amines the $A_{amine,i}$ is nearly zero, since the extinction coefficient of aliphatic amine cation radicals at wavelength i is zero ($\epsilon_{amine,i} = 0$), and the baseline offset (B_{amine}) is the only signal recorded ($A_{amine,i} = l \times \epsilon_{amine,i} \times [\mathrm{amine}^{+\bullet}] + B_{amine}$).[14] Thus, the only adjustable parameter to be fitted is K_{et} (electron-

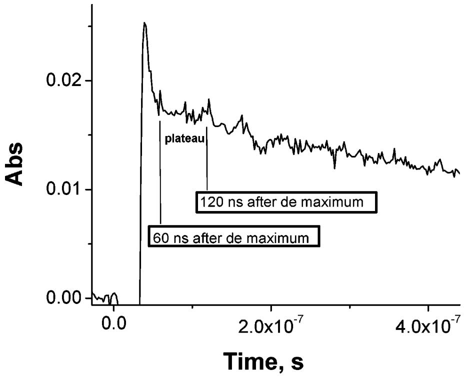


Figure 1. Initial stage of the monitoring of the transient kinetic trace at 495 nm of a HMB /dodecylamine, **8**, solution.

---

(8) Dockery, K. P.; Dinnocenzo, J. P.; Farid, S.; Goodman, J. L.; Gould, I. R.; Todd, W. P. *J. Am. Chem. Soc.* **1997**, *119*, 1876.

(9) Because the concentration of the cosensitizer is much higher than those of the corresponding Ref or amines, a direct electron transfer between them and the sensitizer excited state (A^{+*}) must be negligible. Hence, the concentration of different radical cations should be equal, making it possible to determine their relative extinction coefficient at any wavelength.

(10) (a) $E°$, ($HMB^{+\bullet}/HMB$) = 1.580 V vs SCE in CH_3CN. See Amatore, C.; Lefrou, C. *J. Electroanal. Chem.* **1992**, *325*, 239. (b) $E°$, ($HMB^{+\bullet}/HMB$) = 1.590 V vs SCE in CH_2Cl_2. See Gould, I. R.; Ege, D.; Moser, J. F.; Farid, S. *J. Am. Chem. Soc.* **1990**, *112*, 4290.

(11) The difference in standard potential should be small for equilibrium reasons. Potential peak values obtained electrochemically[7] seem to indicate that the $E°$ can be around 1.50 V vs. SCE. Thus, HMB was used as a Ref compound.[10]

(12) Separated spectra of "pure" Ref compound and amine mixtures were recorded using co-sensitized electron-transfer conditions; hence, equal concentrations of cation radicals were generated.

(13) Equation 2 makes the conventional assumption that concentrations can be used in place of activity coefficients. The neglect of activity coefficients should be inconsequential since the ionic strength of the medium is particularly low and the species on both sides of the equilibrium (eq 1) are expected to be quite similar.

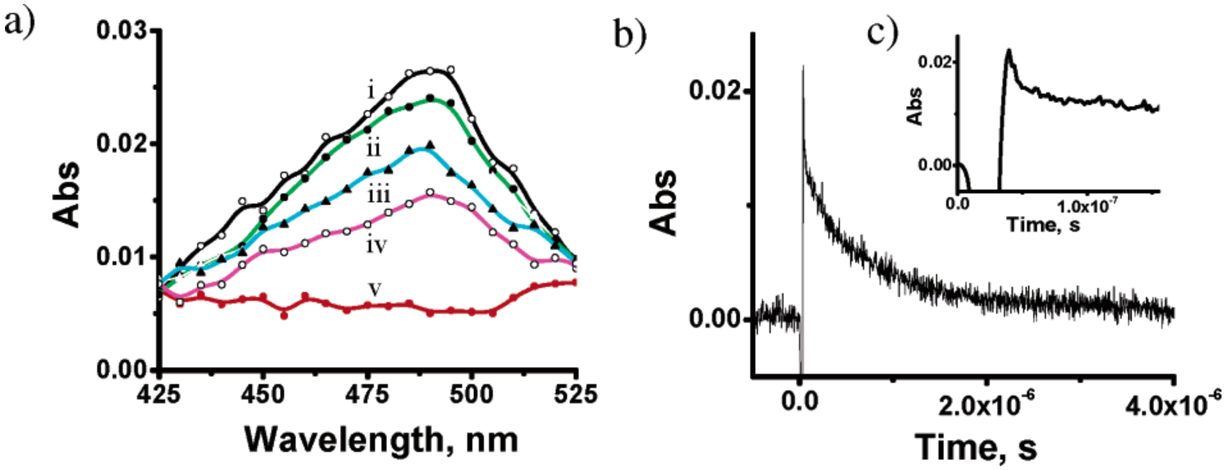


Figure 2. (a) Transient absoption spectra of HMB$^{+\bullet}$ (i) (λ_{max} = 495 nm), pentylamine cation radical (v) **3**$^{+\bullet}$ and the corresponding equilibrium spectra recorded 70 ns after the laser pulse (color lines) in oxygen-saturated CH_3CN. [HMB]/[**3**] ratios: (ii) 50.6 mM/0.6 mM, (iii) 50.3 mM/1.2 mM, (iv) 49.2 mM/2.3 mM. (b) Transient kinetic absorption at 495 nm corresponding to the first addition of amine (i): the entire decay and (c) its initial part (t_{eq}).

Table 1. Standard Potentials (in V vs SCE) for **1**−**12** in CH_3CN and CH_2Cl_2 at 20 °C

amine	Ref compound	$E° = -(RT/F) \ln K_{et}$	$E°$ (amine$^{+\bullet}$/amine)
	CH_3CN (Unbranched Acyclic Amines)		
n-propyl (**1**)	HMB[a] ($E°$ = 1.580 V)	0.063 (±0.003)	1.517 (±0.003)
n-butyl (**2**)	HMB	0.071 (±0.003)	1.509 (±0.003)
n-pentyl (**3**)	HMB	0.080 (±0.002)	1.500 (±0.002)
n-hexyl (**4**)	HMB	0.091 (±0.003)	1.489 (±0.003)
n-heptyl (**5**)	HMB	0.084 (±0.004)	1.496 (±0.004)
n-octyl (**6**)	HMB	0.079 (±0.004)	1.501 (±0.004)
n-decyl (**7**)	HMB	0.077 (±0.005)	1.503 (±0.005)
n-dodecyl (**8**)	HMB	0.080 (±0.005)	1.500 (±0.005)
	CH_3CN (Branched Acyclic Amines)		
isopropyl (**9**)	HMB	0.042 (±0.005)	1.538 (±0.005)
isobutyl (**10**)	HMB	0.065 (±0.004)	1.515 (±0.004)
sec-butyl (**11**)	HMB	0.063 (±0.003)	1.517 (±0.003)
tert-butyl (**12**)	HMB	0.054 (±0.003)	1.526 (±0.003)
	CH_2Cl_2		
n-butyl (**2**)	HMB[a] ($E°$ = 1.590 V)	−0.073 (±0.005)	1.663 (±0.005)
	4,4′-BP[b] ($E°$ = 1.664(5))	−0.001 (±0.002)	1.665 (±0.005)
tert-butyl (**12**)	HMB	−0.055 (±0.005)	1.647 (±0.005)
	4,4′-BP	−0.017 (±0.001)	1.647 (±0.005)

[a] Based on electrochemical data.[8] [b]4,4′-dimethylbiphenyl (4,4′-BP) determined by nanosecond equilibrium measurements.[5]

transfer equilibrium constant), even when only one of the radical cations is detectable (eqs 2 and 3). Finally, once K_{et} is known, the difference between the standard potentials can easily be calculated from eq 4.

Before measuring the absorption spectra along with the transient kinetic traces for the corresponding Ref$^{+\bullet}$, the solutions were purged with O_2 in order to avoid interference caused by the absorption of A$^\bullet$ (λ_{max} 540 nm, in Scheme 1).[5] The lifetime of this radical has previously been measured in dioxygen-saturated CH_3CN, almost completely reacting within 60 ns. Figure 1 shows a transient kinetic trace monitoring at 495 nm where it is possible to distinguish the rapid decay of A$^\bullet$ at ≥60 ns (Figure 1).[14]

2.2. Redox Equilibria with Alkyl Primary Amines: Determination of $E°$ Values in Acetonitrile. Redox equilibrium spectra were recorded for pairs of HMB$^{+\bullet}$ and several alkyl primary amines$^{+\bullet}$ at the appropriate concentration of the neutral species (0.5−50 mM).[15] The approach to equilibrium was followed in each case by monitoring the absorption of the HMB$^{+\bullet}$ at their λ_{max} being the equilibrium time selected ($t_{eq,}$) ~60−120 ns (Figure 1). The UV−vis spectrum is then recorded at the delay time corresponding to the t_{eq} for the pure and mixed (HMB/amine) samples. A typical complete sequence of the observed experimental procedure is shown in Figure 2.

It is important to note that around 5 ns the equilibrium time range became shorter upon each amine addition. This effect can

---

(14) The baseline offset for the Ref and amine radical cation spectra ($B_{reference}$ and B_{amine}) could also contain a small contribution of residual one-electron photosensitizer (A$^\bullet$, λ_{max} 540 nm), which has not been totally quenched with oxygen at the selected t_{eq}. It is important to remark that when the equilibrium experiments were performed under argon atmosphere the same $E°$ values for the selected amines were obtained, although no clean cation radical spectra of HMB were recorded.

(15) Using toluene (C) in high concentration as a codonor (1 M), the "free" toluene cation radical is a powerful one-electron oxidant (2.35 V vs SCE) that can then be used effectively, irreversibly oxidizing the alkyl amines and reference (Ref) that are present at a relatively low concentration (e.g., 0.5−50.0 mM) in solution. The concentration of "free" amine in the stock solution amine was carefully determined using electrochemical techniques, since some of the amine can be protonated in this medium (see: Mann, C. K. *Anal. Chem.* **1964**, *36*, 2424). Moreover, in the range of HMB concentration used, a maximum of 2% can be formed, as a consequence of the formation of this dimer cation radical a 2% error in the determination of K_{et} can occur. Fortunately, this will correspond to a systematic and unaffected error in $\Delta E°$ of 0.0005 V, which will not affect our determinations.

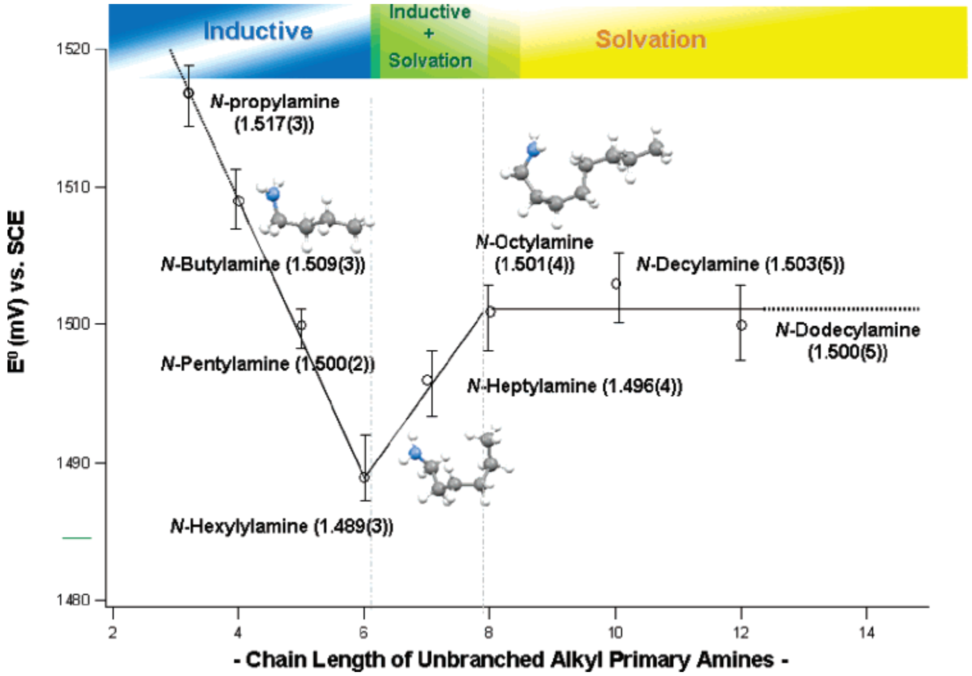


Figure 3. Graphic representation of some of the data given in Table 1. (Inset): B3LYP/6-311G(d,p) calculated structures for the following selected amines $\mathbf{2}^{+\bullet}$, $\mathbf{4}^{+\bullet}$, and $\mathbf{6}^{+\bullet}$. Solvent effects, acetonitrile ($\epsilon = 36.64$), were taken into account using the polarization continuum model (PCM).

be explained by the proton-transfer reaction from the amine cation radicals to the neutral, which seems to be exothermic and reasonably fast[7,16] and should modify the duration of the plateau zone (see Figures 1 and 2c). A plot of pseudo-first-order rate for the decay of hexamethylbenzene cation radical after the equilibrium time as a function of the concentration of added amine demonstrates the reactivity as a base of the neutral pentylamine for the corresponding amine cation radical ($k = 6 \times 10^6$ M^{-1} s^{-1}). Thus, the UV−vis spectrum of the mixture should be recorded when the equilibrium is reached and, of course, before the proton-transfer reaction takes place. Otherwise, the spectrum of HMB$^{+\bullet}$ in the mixture at the t_{eq} will be affected by that reaction, a point that has therefore been carefully addressed and avoided in all these studies (Figure 1).

The $E°$ values for the remaining pairs were obtained in a similar manner, leading to excellent results (Table 1, see Supporting Information for the spectra). The high precision of the method (experimental error less than 6 mV) makes it possible to determine thermodynamically meaningful data, providing some insight into the origin of the different $E°$. For short-chain alkyl primary amines (**1**−**4**) the average differences are ~8 mV. The variation of the standard potential value with the number of carbon atoms appears to be linear, and thus it seems that, in these cases, the methylene group ($-CH_2-$) has an inductive effect, which is responsible for the stabilization of the amine cation radical since the solvation of the amino group should be similar in all these cases.

The comparison of the $E°$ values in CH_3CN between *n*-butylamine, **2**, and *tert*-butyl amine, **12**, shows that the oxidation potential of **2** is lower than that of **12** (17 mV), which obviously contradicts the aforementioned inductive effect. The same result is obtained when comparing the values of *n*-propylamine, **1**, and isopropylamine, **9**. A plausible explanation is related to differences in the solvation environment around the NH_2 group. It seems that each CH_3 branched to the α carbon blocks the accessibility of the solvent to the polar group. Moreover, it appears to be a 9 mV loss of stabilization solvation energy per methyl group bonded to the α carbon ($C_\alpha-(CH_3)_n$ where $n = 1$, 2, or 3)). Substrates **9**−**12** would also present steric solvation inhibition relative to **1** or **2** respectively due to the branched alkyl group.[17]

In order to confirm the aforementioned explanation, equilibrium experiments were performed in a less polar solvent such as CH_2Cl_2. A comparison of the $E°$ values in CH_2Cl_2 and CH_3CN shows that the oxidation potentials of *n*-butylamine and *tert*-butylamine are lower in CH_3CN by 154 and 121 mV, respectively, thus confirming that the differences in the cation radical solvation energies are greater for the *n*-butylamine cation radical than for the *tert*-butylamine cation radical. We can therefore conclude that in CH_2Cl_2 the solvation effect is dramatically minimized, the $E°$ of **12** is smaller than **2**, indicating that the inductive effect of the *tert*-butyl group is again the main effect. To test the internal consistency of the $E°$ values for **2** and **12** obtained in CH_2Cl_2 each amine was studied using two different reference compounds (HMB and 4,4′-BP). As the data in Table 1 show, the two $E°(\mathbf{2})$ and $E°(\mathbf{12})$ values obtained independently from the two references are in excellent agreement.

---

[16] It is possible to calculate the pK_a's in CH_3CN for primary cation radicals and ammonium cations using the standard potentials shown in table 1, being the pK_a ($RNH_2^{+\bullet}$) ≈ 14 and pK_a (RNH_3^+) ≈ 18, respectively.

[17] An analogous effect was found by Ingold and Hughes when they studied the influence of the substituent on the S_N2 reaction rates using neopentyl and ethyl bromides. The steric effect due to the presence of the neopentyl group had a major influence on reaction rates, being the high activation energy value referred to the steric hindrance in the transition state. The larger substituent forces the nucleophile and the leaving group away from their lineal arrangement, see: (a) Dostrovski, I.; Hughes, E. D. *J. Chem. Soc.* **1946**, 157. (b) Dostrovski, I.; Hughes, E. D.; Ingold, C. K. *J. Chem. Soc.* **1946**, 173. (c) de la Mare, P. B. D.; Fowden, L.; Hughes, E. D.; Ingold, C. K.; Mackie, J. D. H. *J. Chem. Soc.* **1955**, 3200. (d) Vayner, G.; Houk, K. N.; Jorgensen, W. L.; Brauman, J. I. *J. Am. Chem. Soc.* **2004**, *126*, 9054.

Note that the standard potentials of **5** and **6** in acetonitrile are indistinguishable within experimental error, whereas for longer, unbranched alkyl primary amines (**5**−**8**) the *E*° rises slightly to 1.500 V, where it remains constant. We suggest that these results could be the consequence of steric inhibition of solvation around the amino group due to a fold of the long alkyl chain following a solvent exclusion mechanism (Figure 3).[17] Since the *E*° value origin of the amines is associated with alkyl chain length, the structures of three "model" amine cation radicals were computed using the B3LYP density functional method and a 6-311G(d,p) basis set.[18] In the case of shorter amine cation radicals, such as $\mathbf{2}^{+\bullet}$, as mentioned earlier, the *E*° values are strongly related to the number of methylene groups. This is in good agreement with the minimum-energy conformation found for those cation radicals where the alkyl chain is mainly extended. Thus, the solvation effect around the polar group should be similar in all these cases. We can conclude that those amines will be located in the "pure" inductive-effect zone (Figure 3). In contrast, longer amine cation radicals, such as $\mathbf{6}^{+\bullet}$, are expected to be in the pure "solvation-effect" zone since the determined *E*° values remain at 1.500 V and are not chain-length dependent. This agrees well with the predicted theoretical structure for $\mathbf{6}^{+\bullet}$, in which the most stable conformation corresponds to a fold ring-shape structure. In those cases, the exclusion of solvent molecules around the polar group would have a major influence on *E*° values, with the inductive effects being almost negligible. Finally, for amine cation radicals with an "intermediate length", such as $\mathbf{4}^{+\bullet}$, a "mix-zone" can be distinguished where the steric hindrance is less important than in $\mathbf{6}^{+\bullet}$, a less folded conformation was found, and the inductive effect is still slightly visible.

3. Summary

The generality of the redox equilibrium methodology makes it possible to determine accurate *E*° even if only one of the two radical cations involved in the electron-transfer equilibrium shows a clean absorption spectrum. Moreover, the determination of the *E*° of alkyl primary amines has been reported for the first time. This versatility and accuracy make it possible to quantify inductive and/or solvation effects in a related family on the basis of their *E*° differences. For "short-chain" alkyl primary amines, where the solvation around the amino group is expected to be the same, differences in *E*° values are mainly due to inductive effects, whereas for "long-chain" amines, those values are strongly related to the steric inhibition of solvation effects. Extension to more sophisticated amines, diamines as well as combinations of electrochemical−photochemical−theoretical data to fully determine the oxidation mechanism of alkyl amines has begun.

4. Experimental Section

4.1. Materials. Anhydrous acetonitrile stored in an inert atmosphere and molecular sieves was purchased from Across. Reference compounds (hexamethylbenzene (HMB) and 4,4′-BP(4,4,-dimethylbiphenyl)) and substrates (alkyl primary amines from **1**−**12**) of the highest available purity were purchased and recrystallized several times before use (solids) or fractionally distilled (liquids).

4.2. Nanosecond Apparatus. A nanosecond Laser Flash Photolysis using an LKS60 instrument from Applied Photophysics. Pulses of ca. 9 ns and energies of 5−7.5 mJ were provided by a Q-switched Nd:YAG laser (Spectron Laser Systems, UK). All experiments were carried out under oxygen and in acetonitrile in quartz cells. The transient spectra were obtained by recording the transient decays at different analysis wavelengths. Typically, the data from two laser pulses at 355 nm (OD = 0.5) were averaged (from two to four times) prior to computer processing. In addition, global analysis of the complete kinetic dataset of the decays was carried out using GLint, which is a form of global analysis developed by Applied Photophysics Ltd. that uses the Marquardt−Levenberg algorithm and four-order Runge−Kutta numerical integration.

4.3. Equilibrium Measurements. *N*-Methylquinolinium hexafluorophosphate (NMQ) solutions (OD = 0.5 at 355 nm) containing 1 M toluene were prepared in anhydrous acetonitrile. Experiments were conducted in quartz cuvettes equipped with high-vacuum stopcocks carrying serum caps. Solvent-saturated dioxygen was bubbled through the solutions for 10−15 min before equilibrium measurements were taken. Initially, separate solutions were prepared with each of the equilibrium components in order to record the spectra of their corresponding cation radicals. Increasing concentrations of the second component were then added to one of the cuvettes from a dioxygen-saturated stock solution via calibrated micropipettes. All equilibrium measurements were made at 20 °C (room temperature). In general, equilibrium measurements were made 70−120 ns after the laser pulse. At the end of each equilibrium experiment the laser power was checked to make sure that it had not changed during the course of the experiment. Equilibrium spectra were fit to equilibrium equations using Igor Pro (version 4.07; Wavemetrics, Inc.). The oxidation potential differences given in Table 1 are averages of two to three independent determinations.

Acknowledgment. We gratefully acknowledge the financial support of the Ministerio de Tecnologia y Ciencia of Spain though projects BQU 2003-05457 and CTQ2006-01040. We are pleased to acknowledge Professor J. P. Dinnocenzo, Department of Chemistry, University of Rochester (NY) for helpful discussions and Dr. C. Wang, Department of Chemistry & Biochemistry (University of Missouri-St. Louis) for preliminary theoretical calculations.

Supporting Information Available: Figures of equilibrium electron-transfer spectra for HMB-**1**−**12** amines. This material is available free of charge via the Internet at http://pubs.acs.org.

JA0656245

---

(18) (a) Dudones, L. P.; Gilpin, R. K. *Langmuir* **1999**, 15, 6901.

(19) Theoretical calculation performed by Dr. C. Wang (Department of Chemistry & Biochemistry (University of Missouri-St. Louis) using B3LYP density functional method and a 6-311G(d,p) basis set which are particularly suitable for cation radicals, see: Bally, T.; Borden, W. T. *Rev. Comput. Chem.* **1999**, *13*, 1.