# Two-Electron Transfer from Potassium Anion to Peroxides: Simultaneous or Stepwise?

**Charles L. Perrin,* Jingtao Wang, and Michael Szwarc**[†]

*Contribution from the Department of Chemistry, University of California-San Diego, La Jolla, California 92093-0358*

*Received October 18, 1999*

**Abstract:** Reaction of the two-electron donor $K^+$Crown $K^-$ with phenylacetyl peroxide produces phenylacetic acid, toluene, bibenzyl, and benzyl phenylacetate. The formation of products derived from benzyl radical shows that some electron transfers must be stepwise and that the second electron transfer, although very exothermic, is fast but not exceedingly so. This conclusion is supported by control experiments with sodium naphthalenide, sodium biphenylide, and NaI as reductants, and with benzoyl peroxide.

## Introduction

Electron-transfer processes play an important role across a wide range of chemistry.[1] Various metals and their derivatives have been used as electron donors.[2] Solutions of alkali metals in THF with a complexant L such as 18-Crown-6 contain not only complexed metal cations but also metal anions (eq 1).[3] Such solutions can be used as strong reducing agents.[4] Reactions of these alkali metal anions with organic substrates such as cyclic ethers,[5] ketones,[6] and halides[7] have recently attracted much attention. Often these alkali metal anions show a distinctive reactivity, different from that of one-electron reducing agents such as the solvated electron. For example, $\beta$-lactones undergo C−C cleavage, rather than the usual C−O,[8] and styrene and methyl methacrylate lead to ethylbenzene and methyl isobutyrate rather than to products from dimerization of the radical anion.[9]

$$2M + L \rightarrow M^+L + M^- \tag{1}$$

The distinctive reactivity of these alkali metal anions $M^-$ is due to their ability to transfer two electrons and produce transient dianions. On transfer of the first electron, the metal atom M remains, and it is still a powerful donor of a second electron. Thus, an organic substrate can accept two electrons, leading to products from organic dianions. Thus, ethylbenzene is produced from the dianion of styrene, which is monoprotonated by solvent and again on workup.

Might the two electrons be transferred simultaneously?[10] This question does not arise for most of the above substrates, where the second electron enters the same antibonding molecular orbital as the first one. The resulting repulsion then makes the second electron transfer much less favorable than the first. However, if a bond cleavage accompanies electron transfer, as perhaps with $\beta$-lactones, the second electron may enter a nonbonding molecular orbital. If so, the second electron transfer may be even more favorable than the first, and it may be transferred simultaneously with the first. Alternatively, the reaction may be viewed as a concerted two-electron transfer analogous to nucleophilic substitutions, but with the electron pair as the nucleophile.

Organic peroxides, particularly diacyl peroxides $(RCO_2)_2$, offer the possibility of simultaneous two-electron reduction. The first electron transfer effects cleavage of the O−O bond (eq 2). Transfer of another electron, from the potassium atom to the radical (eq 3), must be quite exothermic in solution, since a potassium carboxylate is a salt and not a pair of radicals. This second electron transfer should be fast, perhaps even concerted with the first. Indeed, electrochemical reduction of peroxides proceeds by just such an irreversible two-electron process,[11] and the kinetics of reduction of peroxides by hydroquinones follows the Marcus equation for electron transfer, but with a high intrinsic barrier due to the breaking of the O−O bond.[12]

$$(RCO_2)_2 + K^- \rightarrow RCO_2^- + RCO_2\cdot + K\cdot \tag{2}$$

$$RCO_2\cdot + K\cdot \rightarrow RCO_2^- + K^+ \tag{3}$$

The question we address is whether the acetoxy radical is an intermediate in the reaction. If the second electron transfer is

---

[†] Present address: 1176 Santa Luisa Dr., Solana Beach, CA 92975.

[1] Isied, S. S., Ed. *Electron-Transfer Reactions: Inorganic, Organometallic, and Biological Applications*; American Chemical Society: Washington, DC, 1997. Gray, H. B.; Winkler, J. R. *Annu. Rev. Biochem.* **1996**, *65*, 537. Astruc, D. *Electron Transfer and Radical Processes in Transition-Metal Chemistry*; VCH: New York, 1995. Chanon, M.; Rajzmann, M.; Chanon, F. *Tetrahedron* **1990**, *46*, 6193. Eberson, L. E. *Electron-Transfer Reactions in Organic Chemistry*; Springer-Verlag: Berlin, 1987.

[2] Paul, D. E.; Lipkin, D.; Weissman, S. I. *J. Am. Chem. Soc.* **1956**, *78*, 116. Szwarc, M.; Levy, M.; Milkovich, R. *J. Am. Chem. Soc.* **1956**, *78*, 2656. Garst, J. F. *Acc. Chem. Res.* **1971**, *4*, 400. Ohsawa, T.; Mitsuda, N.; Nezu, J.; Oishi, T. *Tetrahedron Lett.* **1989**, *30*, 845.

[3] Dye, J. L.; DeBacker, M. G.; Nicely, V. A. *J. Am. Chem. Soc.* **1970**, *92*, 5226. Dye, J. L. *Prog. Inorg. Chem.* **1984**, *32*, 327.

[4] Jedlinski, Z.; Stolarzewicz, A.; Grobelny, Z.; Szwarc, M. *J. Phys. Chem.* **1984**, *88*, 6094. Jedlinski, Z. *Pure Appl. Chem.* **1993**, *5*, 483. Jedlinski, Z. *Acc. Chem. Res.* **1998**, *31*, 55.

[5] Jedlinski, Z.; Misiolek, A.; Jankowski, A.; Janeczek, H. *J. Chem. Soc., Chem. Commun.* **1991**, 1513.

[6] Szwarc, M.; Jedlinski, Z.; Janeczek, H. *Macromolecules* **1997**, *30*, 4498. Jedlinski, Z.; Kurcok, P.; Adamus, G. *Macromol. Chem.* **1989**, *190*, 61.

[7] Vorbruggen, M.; Maas, M. *Heterocycles* **1988**, *27*, 2659.

[8] Jedlinski, Z.; Kowalczuk, M.; Misiolek, A. *J. Chem. Soc., Chem. Commun.* **1988**, 126. Jedlinski, Z.; Misiolek, A.; Kurcok, P. *J. Org. Chem.* **1989**, *54*, 1500.

[9] Jedlinski, Z.; Czech, A.; Janeczek, H.; Kowalczuk, M. *J. Am. Chem. Soc.* **1995**, *117*, 8678. Jedlinski, Z.; Janeczek, H.; Bosek, I. *J. Org. Chem.* **1999**, *64*, 4956.

[10] Szwarc, M. *Acta Chem. Scand.* **1997**, *51*, 529.

[11] Eberson, L. *Chem. Scr.* **1982**, *20*, 29. Antonovskii, V. L.; Frolova, Z. S.; Schleina, T. T.; Buzlanova, M. M. *J. Gen. Chem. USSR* **1969**, *39*, 250.

[12] Adam, W.; Schönberger, A. *Chem. Ber.* **1992**, *125*, 2149.

10.1021/ja9937369 CCC: $19.00

concerted with the first (eq 4), there is no intermediate. To test for an intermediate, it is necessary to use a reaction that traps it before the second electron is transferred.

$$(RCO_2)_2 + K^- \rightarrow 2\ RCO_2^- + K^+ \qquad (4)$$

Such a reaction is the decarboxylation of phenylacetoxy radical (eq 5). This radical is unusual in that its $CH_2-CO_2$ bond has a *negative* bond-dissociation energy, reflecting a cleavage that is exothermic by 23 kcal/mol.[13] Consequently, this acetoxy radical is very unstable, with a lifetime of 200−600 ps in polar solvents,[14] where decarboxylation is slower,[15] of 55 ps as judged from a related radical,[16] or of only 3.6 ps at 343 K in $CCl_4$.[17] Indeed, thermal fragmentation of phenylacetyl peroxide or *tert*-butyl phenylperacetate bypasses the radical and instead proceeds by concerted cleavage of C−C and O−O bonds.[18] Thus, if electron transfer is stepwise, products from benzyl radical should be detectable. This test has previously been used to distinguish homolytic and heterolytic mechanisms for reaction of peracids with two different iron oxo species.[19] It is analogous to the use of radical clocks to detect the intermediacy of short-lived radicals that undergo bond cleavage by ring opening.[20]

$$PhCH_2CO_2\cdot \rightarrow PhCH_2\cdot + CO_2 \qquad (5)$$

We now report the reaction of phenylacetyl peroxide with potassium anion. As controls we include reactions of benzoyl peroxide, aromatic radical anions, and iodide ion. Our experimental results indicate that electron transfer from the metal anion to peroxide occurs in two steps.

## Experimental Section

**Instrumentation and Analytical Method.** Reaction products were analyzed on a Varian 3700 gas chromatograph (GC) with a column of 10% SP2250 on 100/120 Supelcoport and a 30 $cm^3$/min helium flow.[21] The temperatures of injector and FID detector were 250 and 310 °C, respectively. For analysis of products from phenylacetyl peroxide the oven temperature was initially held at 30 °C for 7 min, ramped at 17 °C/min to 220 °C (initially at 65 °C and ramped at 7 °C/min for trimethylsilyl phenylacetate), and held there for 10 min. For analysis of products from benzoyl peroxide the column was held for 2 min at 105 °C, then ramped at 15 °C/min to 220 °C. The instrument response was calibrated with weighed amounts of authentic substances plus mesitylene as internal standard.

**Materials.** Sodium or potassium metal was rinsed in hexane and in dry ether, and the surface was removed and discarded. 18-Crown-6 (Aldrich) was recrystallized from acetonitrile, vacuum distilled, and dried in a vacuum.[22] Naphthalene was purified by vacuum sublimation. Biphenyl was recrystallized from methanol, vacuum distilled, and dried over $P_2O_5$ in a vacuum. Tetrahydrofuran (THF) was refluxed over $CaH_2$ for 48 h, distilled, stored over sodium benzophenone under argon, and freshly distilled before use. Commercially available 70% benzoyl peroxide (Aldrich) was recrystallized from chloroform/methanol.

**Potassium-18-Crown-6 ($K^+$Crown $K^-$, 0.4 M in THF).** To a flask purged with argon was added 0.109 g (0.4 mmol) of 18-Crown-6, followed by 1 mL of THF. To the homogeneous solution a freshly cut slice of excess potassium metal was added at room temperature under argon, and a blue color appeared immediately. After 15 min the solution was cannulated under argon pressure into a dry flask.

**Sodium Naphthalenide ($Na^+C_{10}H_8^-$, 0.88 M in THF).**[23] Naphthalene (0.113 g, 0.88 mmol) was dissolved in 1 mL of THF under argon. To the solution an excess of freshly cut metallic sodium was added. A dark green solution formed gradually. The mixture was stirred at room temperature for 2 h and cannulated under argon pressure into a dry flask.

**Sodium Biphenylide ($Na^+Ph_2^-$, 0.85 M in THF).** This solution was prepared in the same way as for sodium naphthalenide. A green-blue solution was obtained.

**Phenylacetyl Peroxide.**[24] To 0.1 g of phenylacetyl chloride cooled in an ice−salt bath was added 0.15 mL of 30% $H_2O_2$, followed by NaOH solution (0.14 g in 1 mL $H_2O$, cooled to freezing). The mixture was shaken near but below 0 °C. After several minutes white flakes were produced. The product was filtered through a precooled funnel and washed with ice water and cold methanol. The peroxide was quickly transferred with a porcelain spatula into 1 mL of THF at −78 °C. The amount of peroxide was determined from the weights before and after. Reaction with excess potassium iodide and GC analysis (see below) showed that the purity is >96%.

**Typical Procedures for Peroxide Reductions. Reaction of Phenylacetyl Peroxide with $K^+$Crown $K^-$.** To 1 mL of potassium-18-Crown-6 solution (0.4 M) at −78 °C under argon was added phenylacetyl peroxide (28 mg, 0.10 mmol) in 1 mL of THF. The mixture was stirred with a glass-coated magnetic stirring bar. The blue color persisted for 1 h, verifying a stable excess of reductant. The reaction was then quenched by adding methanol. A sample of the resulting yellow solution was analyzed for neutrals by GC, with a weighed amount of mesitylene as internal standard. The solution was acidified by stirring for 30 min with cation-exchange resin. Solvents were removed by rotary evaporation. The residue was dissolved in 1:1 ethyl acetate−ethyl ether and was dried, filtered, and evaporated under reduced pressure and then in a vacuum desiccator. The residue was stirred for 24 h with 1 mL of hexamethyldisilazane and 0.34 mL of chlorotrimethylsilane in 1 mL of pyridine[25] and then analyzed by GC, with mesitylene as internal standard.

**Reaction of Phenylacetyl Peroxide with $Na^+C_{10}H_8^-$.** The peroxide (30 mg, 0.11 mmol) was added with stirring to 1 mL of the metal complex (0.88 M). The dark green color persisted, verifying an excess of reductant. The reaction was quenched after 1 h by the addition of methanol. The system was treated and analyzed by GC as above.

**Reaction of Phenylacetyl Peroxide with $Na^+Ph_2^-$.** The peroxide (18 mg, 0.07 mmol) was added with stirring to 1 mL of the metal complex solution (0.85 M). After 1.6 h methanol was added to the mixture, which was treated and analyzed by the same method as above.

**Reaction of Phenylacetyl Peroxide with NaI.** A 4-fold excess of NaI was dissolved in THF, cooled to −78 °C, and then added under argon to cold phenylacetyl peroxide with stirring. The solution turned yellow immediately. After 30 min, methanol was added, and the sample was analyzed by GC.

**Reactions of Benzoyl Peroxide.** The method described above was used for reactions of benzoyl peroxide with $K^+$Crown $K^-$ and $Na^+Ph_2^-$, but not $Na^+C_{10}H_8^-$ because naphthalene interferes with the GC analysis of benzoic acid. The peroxide was either added as a solid or dissolved in THF and then added. Reactions were carried out in an ice−salt bath (−15 °C) under argon with a 2-fold excess of alkali metal complexes. After 1 h the reaction was quenched by adding methanol, and the mixture was acidified with HCl. The organic solvents were removed under vacuum, and the remaining aqueous layer was extracted with

---

[13] Rembaum, A.; Szwarc, M. *J. Am. Chem. Soc*. **1955**, *77*, 3486. Luo, Y.-R.; Holmes, J. L. *J. Phys. Chem.* **1994**, *98*, 303.

[14] Bockman, T. M.; Hubig, S. M.; Kochi, J. K. *J. Org. Chem.* **1997**, *62*, 2210. Hilborn, J. W.; Pincock, J. A. *J. Am. Chem. Soc.* **1991**, *113*, 2683.

[15] Tateno, T.; Sakuragi, H.; Tokumaru, K. *Chem. Lett.* **1992**, 1883.

[16] Falvey, D. E.; Schuster, G. B. *J. Am. Chem. Soc.* **1986**, *108*, 7419.

[17] Skakovskii, E. D.; Rykov, S. V.; Turetskaya, E. A.; Gurinovich, N. A.; Ol'dekop, Yu. A. *Vestsi Akad. Navuk BSSR, Ser. Khim. Navuk* **1982**, 34; *Chem. Abstr*. **1983**, *98*, 52972m.

[18] Bartlett, P. D.; Leffler, J. E. *J. Am. Chem. Soc.* **1950**, *72*, 3030.

[19] Stassinopoulos, A.; Caradonna, J. P. *J. Am. Chem. Soc.* **1990**, *112*, 7071.

[20] Horner, J. H.; Tanaka, N.; Newcomb, M. *J. Am. Chem. Soc.* **1998**, *120*, 10379.

[21] Crippen, R. C. *GC/LC, Instruments, Derivatives in Identifying Pollutants and Unknowns*; Pergamon Press: 1983.

[22] Dye, J. L. *J. Phys. Chem.* **1980**, *84*, 1084.

[23] Scott, N. D.; Walker, J. F.; Hansley, V. L. *J. Am. Chem. Soc.* **1936**, *58*, 2442.

[24] Hey, D. H.; Walker, E. W. *J. Chem Soc*. **1948**, 2213.

[25] Dalgliesh, C. E.; Horning, E. C.; Horning, M. G. *Biochem. J*. **1966**, *101*, 792.

**Table 1.** Products (mol %) from Reaction of Phenylacetyl Peroxide with Two-Electron Reductants

| reductant | $K^+$Crown $K^-$ | | | | | NaI |
|---|---|---|---|---|---|---|
| $M_{\text{reductant}}$ | 0.12 | 0.20 | 0.30 | 0.20 | 0.20 | 0.18 |
| $M_{\text{peroxide}}$ | 0.045 | 0.045 | 0.045 | 0.05 | 0.075 | 0.045 |
| toluene | 50 | 53 | 53 | 53 | 51 | <2 |
| phenylacetic acid | 118 | 120 | 125 | 137 | 108 | 192 |
| bibenzyl | 1 | 7 | <1 | <1 | 2 | <1 |
| benzyl phenylacetate | 12 | 6 | 10 | 4 | 17 | <1 |

**Table 2.** Products (mol %) from Reaction of Phenylacetyl Peroxide with One-Electron Reductants

| reductant | $Na^+Ph_2^-$ | | $Na^+C_{10}H_8^-$ | | | | |
|---|---|---|---|---|---|---|---|
| $M_{\text{reductant}}$ | 0.42 | 0.42 | 0.20 | 0.44 | 0.44 | 0.44 | 0.80 |
| $M_{\text{peroxide}}$ | 0.048 | 0.022 | 0.047 | 0.034 | 0.055 | 0.09 | 0.045 |
| toluene | 83 | 88 | 77 | 86 | 80 | 76 | 82 |
| phenylacetic acid | 99 | 103 | 95 | 99 | 105 | 102 | 97 |
| bibenzyl | 6 | 1 | 5 | 6 | 7 | 7 | 9 |
| benzyl phenylacetate | <1 | <1 | 4 | <1 | <1 | 2 | <1 |

**Table 3.** Products (mol %) from Reduction of Benzoyl Peroxide

| reductant | $K^+$Crown $K^-$ | $Na^+Ph_2^-$ |
|---|---|---|
| phenyl benzoate | 3 | 3 |
| benzoic acid | 184 | 180 |

ether. The ether phase was separated and evaporated. The products and a weighed amount of mesitylene as internal standard were dissolved in THF and analyzed by GC.

## Results

The product analyses, averaged over three experiments, are listed in Tables 1−3. Naphthalene or biphenyl was also detected from those reactions using $Na^+C_{10}H_8^-$ or $Na^+Ph_2^-$ as reductant. The data are given as mol % of each product, based on peroxide. For those products with two phenyl groups the maximum possible yield is 100%, but for those with only one phenyl the maximum is 200%. Repeat experiments indicate that yields are reproducible to ±3%, although analysis for phenylacetic acid was more erratic.

Qualitatively, it is clear that toluene, bibenzyl, and benzyl phenylacetate are all produced from phenylacetyl peroxide, along with phenylacetic acid, which is the major product and the only product when NaI is the reductant. The mass balance of phenyl groups is good, always ≥95%. Likewise, in the reaction of benzoyl peroxide the major product is benzoic acid, but there is some phenyl benzoate, and the mass balance is near 95%.

## Discussion

The formation of toluene, bibenzyl, and benzyl phenylacetate from phenylacetyl peroxide is conclusive evidence for the intermediacy of phenylacetoxy radical. If two-electron transfer had occurred, bypassing this radical, then the only product would have been phenylacetate anion, which would analyze as 200% phenylacetic acid. Instead there is an average of only 122 ± 11%.

The remainder of the phenyl groups were converted to the other three products. Those arise by decarboxylation to benzyl radical (eq 5), which reacts with the potassium atom (eq 6), dimerizes (eq 7), or enters into an induced decomposition with unreacted peroxide (eq 8), or perhaps the peroxide acylates benzyl anion. Thus, the formation of toluene, bibenzyl, and benzyl phenylacetate, all derivable from benzyl radical, conclusively indicates the intermediacy of phenylacetoxy radical.

$$PhCH_2^{\bullet} + K^{\bullet} \rightarrow PhCH_2K\ (\rightarrow PhCH_3,\ \text{ester}) \qquad (6)$$

$$2\ PhCH_2^{\bullet} \rightarrow PhCH_2CH_2Ph \qquad (7)$$

$$PhCH_2^{\bullet} + PhCH_2COO{-}OCOCH_2Ph \rightarrow PhCH_2COOCH_2Ph + PhCH_2CO_2^{\bullet} \qquad (8)$$

The additional 22% of phenylacetic acid, beyond the first equivalent from the first electron, represents phenylacetoxy groups that did not decarboxylate. The variability is large (±11%), but the data show conclusively that neither 100% nor 200% phenylacetic acid is formed. It is unlikely that the extra 22% arises from transfer of a second electron to the peroxide before it cleaves, since the O−O bond is weak enough that the radical anion should cleave more readily than it can be converted to a dianion. We cannot exclude the possibility that 22% of the reaction occurs by a concerted two-electron transfer to the peroxide (eq 4), perhaps via an $S_N2$ (or $S_N2'$) reaction at oxygen with the electron pair as the nucleophile. However, a more precedented mechanism is simply transfer of a second electron to the phenylacetoxy radical (eq 9) competitive with the highly exothermic decarboxylation (eq 5). We may further speculate whether the efficiency of the second electron transfer might be governed by the position of the potassium atom relative to the acetoxy radical in the cage where they are created. Regardless of the mechanism for formation of the additional phenylacetic acid, the key result is the detection of the other products, derivable from benzyl radical.

$$PhCH_2CO_2^{\bullet} + K^{\bullet} \rightarrow PhCH_2CO_2^-\ K^+ \qquad (9)$$

Reaction of phenylacetyl peroxide with the sodium salts of aromatic radical anions naphthalenide or biphenylide leads to these same products, but in somewhat different proportions. The amounts of toluene and bibenzyl are somewhat greater and the amount of benzyl phenylacetate is lower. The key difference is that the amount of phenylacetic acid is only 100 ± 3.5%. Such a yield is to be expected, since one-electron reduction produces one phenylacetate anion and one phenylacetoxy radical (eq 10). This latter immediately decarboxylates before it can encounter a second electron donor (eq 11, analogous to eq 6). Even if the second electron transfer requires no activation energy, the average waiting time before encounter is >1 ns at the concentrations used here. This is long compared to the time for decarboxylation.[14,16−17]

$$ArH^{\bullet -} + (PhCH_2CO_2)_2 \rightarrow PhCH_2CO_2^- + PhCH_2CO_2^{\bullet} \rightarrow PhCH_2^{\bullet} + CO_2 \qquad (10)$$

$$PhCH_2^{\bullet} + ArH^{\bullet -} \rightarrow PhCH_2^- + ArH \qquad (11)$$

There are slight variations of product ratios with concentrations of reactants. These can be attributed to the partitioning of benzyl radical, but only qualitatively. Increasing the ratio of peroxide to reductant leads to greater amounts of benzyl phenylacetate, as expected for competition between an induced decomposition (eq 8) and reduction. There is a corresponding decrease in the amount of toluene in reactions with $ArH^{\bullet -}$. In reactions with $K^-$ the amount of toluene is constant, since this represents radical that decarboxylates (eq 5) and accepts a second electron before it escapes the cage (eq 6).

Control experiments with benzoyl peroxide show that the dominant product with either kind of reductant is benzoic acid. Decarboxylation of benzoyloxy radical, $PhCO_2\bullet$, followed by induced decomposition of peroxide, is not competitive with transfer of a second electron, either from K atom in the cage or from another $ArH^{\bullet -}$.

The reaction of phenylacetyl peroxide with sodium iodide results in only phenylacetic acid. This control experiment verifies that the other products cannot have been derived from thermal decomposition of the peroxide. The mechanism is an $S_N2$ (or $S_N2'$) reaction at oxygen (eq 12), followed by another at iodine (eq 13).[26] In principle, reaction of peroxide with $K^-$ could have been analogous, but it is not, except perhaps for 22%.

$$(RCO_2)_2 + I^- \rightarrow RCO_2^- + RCOOI \qquad (12)$$

$$RCOOI + I^- \rightarrow RCO_2^- + I_2 \qquad (13)$$

**Acknowledgment.** This work was supported in part by the National Institutes of Health (Research Grant HL13581).

JA9937369

---

[26] Tokumaru, K. *Chem. Lett.* **1992**, 523.