

Charge-Transfer Quenching of Excited Ketones by Selenides

Yuko Yamazaki, Takayuki Nakamura,
and Tadashi Hasegawa*

Department of Chemistry, Tokyo Gakugei University,
4-1-1 Nukuikitamachi, Koganei, Tokyo 184-8501

Received May 7, 2003; E-mail: tadashi@u-gakugei.ac.jp

Diphenyl selenide ($k_q = 2.5 \times 10^9 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$) and selenoxide (2.5×10^8) quenched the Type II reaction of butyrophenone through a charge-transfer process more efficiently than the corresponding sulfide (1.5×10^8) and sulfoxide. The irradiation of 2-(benzylseleno)ethyl benzoylacetate gave bis[2-(benzoylacetoxo)ethyl] diselenide and 1,2-diphenylethane.

Quenching of excited molecules is an important process in organic photochemistry. Sulfides quench excited ketones via a charge-transfer (CT) process.^{1,2} Little attention has been focused on the quenching ability of simple selenides and selenoxides. We report here on the CT quenching of photo-reactions of ketones by selenides.

When diphenyl selenide was used as a quencher, a Stern–Volmer plot for the Type II reaction of butyrophenone in benzene showed a linear relationship with a slope of $k_q\tau$ ($326 \text{ mol}^{-1} \text{ dm}^3$). The quenching rate constant (k_q) was calculated to be $2.5 \times 10^9 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$, assuming that the lifetime (τ) of the n,π^* triplet state of butyrophenone is $1.3 \times 10^{-7} \text{ s}$.³ The $k_q\tau$ and k_q values for diphenyl sulfide were also determined to be $20 \text{ mol}^{-1} \text{ dm}^3$ and $1.5 \times 10^8 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$, respectively. Because the ionization potential of selenium is smaller than that of sulfur, quenching by the selenide would involve the CT process.

The feasibility of the CT interaction can be estimated by using the Rehm–Weller equation:⁴

$$\Delta G = -E^* + 96.48 \cdot \{E_{\text{ox}}(D) - E_{\text{red}}(A)\} - C \quad (1)$$

The term C , for taking into account the electrostatic energy in a solvent, can be calculated from the following equation:⁵

$$C = \frac{96.48e^2N}{4\pi\epsilon_0a} \left(\frac{1}{\epsilon} - \frac{2}{37.5} \right) \quad (2)$$

Because the encounter distance (a) is 0.7 nm^5 and the relative dielectric constant (ϵ) is 2.292 for benzene,⁶ the C value for benzene is $75.98 \text{ kJ mol}^{-1}$. The reduction potential ($E_{\text{red}}(A)$) of butyrophenone was assumed to be the same as that of valerophenone (-2.07 V).⁷ Because the Type II photoreaction of butyrophenone proceeds from its n,π^* triplet excited state⁸ and the excitation energy E^* in Eq. 1 has been proposed to be the triplet energy of ketone in the excited CT complex formation between a ketone and an electron donor,⁹ the triplet energy of butyrophenone in benzene ($308.4 \text{ kJ mol}^{-1}$)⁸ was used for the excitation energy. The oxidation potential ($E_{\text{ox}}(D)$) of diphenyl selenide and sulfide were determined to be 1.14 and 1.51 V, respectively, from their cyclic voltammograms. The free-energy changes (ΔG) in the CT quenching of the Type II reaction of butyrophenone by diphenyl selenide and sulfide in benzene were estimated to be -74.64 and $-38.95 \text{ kJ mol}^{-1}$, respectively. Dibutyl sulfide quenches triplet butyrophenone via a CT process.² Because the oxidation potential of the sulfide is ca. 1.8 V,¹ ΔG for the CT quenching by the sulfide is ca. $-10.9 \text{ kJ mol}^{-1}$. These results support the idea of CT quenching of the Type II reaction by diphenyl selenide and sulfide (Table 1).

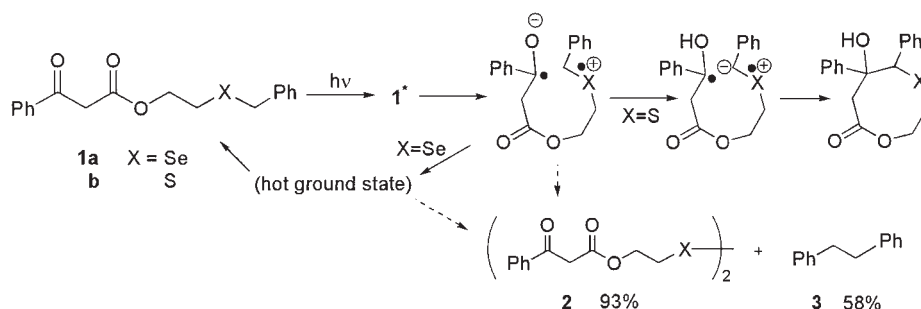
The $k_q\tau$ and k_q values of diphenyl selenoxide were also determined to be $33 \text{ mol}^{-1} \text{ dm}^3$ and $2.5 \times 10^8 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$, respectively. Because the oxidation potential of the selenoxide was 2.05 V, ΔG in the quenching of the Type II reaction was estimated to be $13.18 \text{ kJ mol}^{-1}$. The triplet energy of the selenoxide was determined to be $351.9 \text{ kJ mol}^{-1}$ from its phosphorescence spectrum measured at 77 K in EPA. This value is 39.4 kJ mol^{-1} higher than the triplet energy of butyrophenone ($312.5 \text{ kJ mol}^{-1}$ in EPA at 77 K).¹⁰ Each 5.9 kJ mol^{-1} of endothermicity in an energy-transfer step occurring at near 25°C slows down the rate by a factor of 10, and essentially no quenching of donor triplets occurs when the triplet energy of a donor is less than that of an acceptor by more than several times of 4.2 kJ mol^{-1} .¹¹ These results indicate that the quenching by diphenyl selenoxide involves a CT process.

Intramolecular CT quenching would occur in a molecule having both ketone and selenide chromophores, and proton transfer may follow the CT interaction. We recently reported that 2-(alkylthio)ethyl benzoylacetates underwent photocyclization via remote proton transfer.¹² However, the irradiation of 2-(benzylseleno)ethyl benzoylacetate (**1**) in benzene did not give cyclization products (Scheme 1). The oxidation poten-

Table 1. Kinetic Parameters for the Type II Reaction of Butyrophenone, Oxidation Potential of Quenchers, and Free Energy Change for the CT Quenching of the Type II Reaction

Quenchers	$k_q\tau^{\text{a)}}$ /mol ⁻¹ dm ³	$k_q/10^9 \text{ mol}^{-1} \text{ dm}^3 \text{ sec}^{-1}$	E_{ox}/V	$\Delta G/\text{kJ mol}^{-1}$
2,5-Dimethyl-2,4-hexadiene	660 ^{b)}	5.1		
Diphenyl selenide	326	2.5	1.14	-74.64
Diphenyl sulfide	20	0.15	1.51	-38.95
Diphenyl selenoxide	33	0.25	2.05	13.18
Diphenyl sulfoxide	0.2 ^{c)}	0.0015	2.10	17.99
Dibutyl sulfide	45 ^{c)}	0.35	ca. 1.8 ^{d)}	-10.9

a) In benzene. b) Ref. 3 ($\tau = 1.3 \times 10^{-7} \text{ s}$). c) Ref. 2. d) Ref. 1.



Scheme 1.

tial of **1** was determined to be 1.52 V from its cyclic voltammogram. This value is nearly equal to that of diphenyl sulfide, and indicates that the intramolecular CT interaction in **1** is energetically allowed to occur. Back electron transfer from the ketyl anion radical part to the selenide cation radical part in the CT intermediate produced from **1** should occur much faster than intramolecular proton transfer.

In conclusion, selenides act as more effective CT quenchers, but less efficient reducing agents than the corresponding sulfides.

Experimental

The IR spectra were recorded with a JASCO IR Report-100 spectrometer. The ^1H NMR spectra were measured with a JEOL FX-90Q spectrometer using tetramethylsilane as an internal standard. An Ushio 450-W high-pressure mercury lamp was used as an irradiation source. Phosphorescence spectra were recorded with a HITACHI F4500 spectrometer.

Quenching Rate Determination. Benzene solutions of butyrophenone (ca. 0.05 or 0.1 mol dm $^{-3}$) containing a known concentration of hexadecane (ca. 0.005 mol dm $^{-3}$) as a calibrant and appropriate concentrations of a quencher were placed in 150 $\times$ 15 mm Pyrex culture tubes. The tubes were degassed by three freeze-pump-thaw cycles and then sealed. Irradiation was performed on a 'merry-go-round' apparatus with an Ushio 450-W high-pressure mercury lamp. A potassium chromate filter solution was used to isolate the 313 nm line. Analyses of the irradiated samples were performed on a Shimadzu GC-8A gas chromatograph equipped with a flame ionization detector, which was connected to a Shimadzu C-R6A Chromatopac integrator, using a 2 m column containing 15% propylene glycol succinate on Unipore B.

Preparation of 2-(Benzylseleno)ethyl Benzoylacetate (1). Ethyl 2-benzoylacetate (0.97 g, 5 mmol), 2-benzylselenoethanol (1.14 g, 5 mmol), and a small amount of *p*-toluenesulfonic acid were dissolved in 20 dm 3 of benzene. The mixture was placed in a 50-dm 3 round-bottomed flask and refluxed for 67 h. After removal of the solvent under reduced pressure, the residue was chromatographed on a silica-gel column. Elution with hexane–acetone (v/v = 8/1) gave 1.60 g (84%) of **1** as a pink viscous oil. **1**: IR (neat) 1625, 1685, and 1740 cm $^{-1}$; ^1H NMR (CDCl $_3$) δ 2.65 (1.4H, t, J = 6.6 Hz, SeCH $_2$), 2.73 (0.6H, t, J = 6.2 Hz, SeCH $_2$), 3.79 (1.4H, s, CH $_2$), 3.98 (2H, s, CH $_2$ Ph), 4.20 (0.6H, t, J = 6.2 Hz, OCH $_2$), 4.28 (1.4H, t, J = 6.6 Hz, OCH $_2$), 5.65 (0.3H, s, C=CH), 7.3–7.8 (8H, m, aromatic), 7.9–8.1 (2H, m, aromatic), and 12.46 (0.3H, s, OH). Found: C, 59.66; H, 5.00%. Calcd for C $_{18}$ H $_{18}$ O $_3$ Se: C, 59.84; H, 5.02%.

Irradiation of 2-(Benzylseleno)ethyl Benzoylacetate (1). A

solution of **1** (0.53 g, 1.5 mmol) in 50 cm 3 of benzene was placed in a Pyrex vessel and irradiated for 15 h under nitrogen with a 450-W high-pressure mercury lamp. After removal of the solvent, the residue was chromatographed on a silica-gel column. Elution with hexane–acetone (v/v = 3/1) gave 0.10 g of the unreacted starting material **1**, 0.30 g (93%) of bis[2-(benzoylacetoxylethyl)] diselenide (**2**) and 0.06 g (58%) of 1,2-diphenylethane (**3**). The structure of **3** was determined by a direct comparison with a commercially available material. **2**: mp 53.5–54.5 $^{\circ}\text{C}$; IR (KBr) 1620, 1680, and 1740 cm $^{-1}$; ^1H NMR (CDCl $_3$) δ 3.09 (3.2H, t, J = 7.1 Hz, 2 $\times$ SeCH $_2$), 3.14 (0.8H, t, J = 6.2 Hz, 2 $\times$ SeCH $_2$), 4.01 (3.2H, s, 2 $\times$ CH $_2$), 4.43 (3.2H, t, J = 7.1 Hz, 2 $\times$ OCH $_2$), 4.44 (0.8H, t, J = 6.2 Hz, 2 $\times$ OCH $_2$), 4.50 (0.4H, s, C=CH), 7.3–7.5 (6H, m, aromatic), 7.9–8.0 (4H, m, aromatic), and 12.42 (0.4H, s, OH). Found: C, 48.68; H, 4.11%. Calcd for C $_{22}$ H $_{22}$ O $_6$ Se $_2$: C, 48.90; H, 4.10%.

Cyclic Voltammetry. A three-electrode arrangement with the saturated calomel electrode (SCE) as a reference, a platinum coil as a counter electrode, and a platinum disc as a working electrode was used. Dry acetonitrile containing 1 mol dm $^{-3}$ of Et $_4$ NClO $_4$ was used as the supporting electrolyte solution. Experiments were performed at 25 $^{\circ}\text{C}$ in solutions deaerated by passing argon. The peak potential values are those obtained at a sweep rate of 100 mV s $^{-1}$.

References

- 1 J. B. Guttenplan and S. G. Cohen, *J. Org. Chem.*, **38**, 2001 (1973).
- 2 P. J. Wagner and M. J. Lindstrom, *J. Am. Chem. Soc.*, **109**, 3057 (1987).
- 3 P. J. Wagner and A. E. Kempainen, *J. Am. Chem. Soc.*, **94**, 7495 (1972).
- 4 D. Rehm and A. Weller, *Isr. J. Chem.*, **8**, 259 (1970).
- 5 J. Mattary, J. Runsink, J. Gersdorf, T. Rumbach, and C. Ly, *Helv. Chim. Acta*, **69**, 442 (1986).
- 6 J. A. Dean, "Lange's Handbook of Chemistry," 15th ed, McGraw Hill, New York (1999), 5.105.
- 7 P. J. Wagner and E. J. Siebert, *J. Am. Chem. Soc.*, **103**, 7329 (1981).
- 8 P. J. Wagner, M. J. Thomas, and E. Harris, *J. Am. Chem. Soc.*, **98**, 7675 (1976).
- 9 J. B. Guttenplan and S. G. Cohen, *J. Am. Chem. Soc.*, **94**, 4040 (1972).
- 10 J. N. Pitts, Jr., D. R. Burley, J. C. Mani, and A. D. Broadbent, *J. Am. Chem. Soc.*, **90**, 5902 (1968).
- 11 N. J. Turro, "Modern Molecular Photochemistry," Benjamin/Cummings, Menlo Park (1978), Chap. 9.
- 12 Y. Yamazaki, T. Miyagawa, and T. Hasegawa, *J. Chem. Soc., Perkin Trans. 1*, **1997**, 2979.