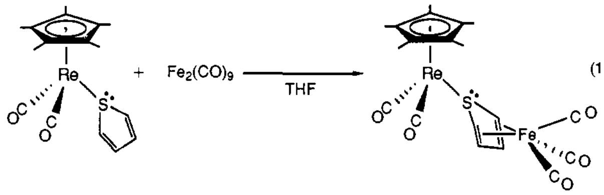
the solution color changes from orange-yellow to dark purple. Evaporation of the solution under vacuum and chromatography of the residue on neutral alumina in CH_2Cl_2/hexanes (1:4) give $Cp^*(CO)_2Re(\mu\text{-}T)Fe(CO)_3$ (**2**) in the yellow band, which upon slow evaporation yields (59%) **2** as air-stable, yellow crystals, which were fully characterized.[12] Thus, the reaction proceeds as in eq 1.



(1)

1 **2**

An X-ray diffraction study[13] shows that **2** contains a bridging thiophene ligand that is coordinated to the Re atom via the sulfur and to the Fe through the four carbons of the diene system. The sulfur is pyramidal as indicated by the angle (125°) between the Re–S vector and the vector from S to the midpoint of the line from C(2) to C(5). The longer distances for C(2)–C(3) (1.458 (8) Å) and C(4)–C(5) (1.427 (8) Å) as compared to that for C(3)–C(4) (1.379 (9) Å) are often found in η^4-1,3-diene complexes;[14] this pattern of C–C bond distances is similar to that found in the S-coordinated thiophene in thiaporphyrin complexes[11] but is just the opposite of that in free thiophene, where C(2)–C(3) and C(4)–C(5) are shorter (1.37 Å) than C(3)–C(4) (1.42 Å),[15] and that in $(C_5H_4CH_2C_4H_3S)Ru(PPh_3)_2^+$.[8] The C(2)–S and C(5)–S distances (1.807 (6), 1.802 (5) Å) are substantially longer than the corresponding distances (1.715 Å)[15] in free thiophene, and the C(2)–S–C(5) angle (82.3°) is much smaller than in thiophene (92°). The thiophene ring is folded with an angle of 36.9 ± 0.4° between the C(2)–C(3)–C(4)–C(5) and C(2)–S–C(5) planes. In general, the geometry (the fold at the C(2)–C(5) line, the long C–S bonds, and the small C(2)–S–C(5) angle of the thiophene) in **2** is different from that of free thiophene[15] and the S-coordinated thiophene in $(C_5H_4CH_2C_4H_3S)Ru(PPh_3)_2^+$[8] but very similar to that of the η^4-thiophene ligand in $Cp^*Ir(\eta^4\text{-}T)$[16] and $Cp^*Ir(\eta^4\text{-}T{\cdot}BH_3)$ (in which the BH_3 is coordinated to the sulfur).[17]

It is interesting that the ν(CO) values for the $Cp^*(CO)_2Re$ group in **2** (1922, 1862 cm^{-1}) are lower than those in **1** (1934, 1874 cm^{-1}), which means that the thiophene sulfur is a better donor to Re when the thiophene is η^4-coordinated to $Fe(CO)_3$. This is consistent with the previous observation[16] that the thiophene sulfur in $Cp^*Ir(\eta^4\text{-}T)$ is a stronger Lewis base toward BH_3 than free thiophene or even Me_2S. Presumably the η^4 coordination of thiophene to a metal separates the diene and sulfur segments of the thiophene and drastically reduces the delocalization of electron density from the sulfur to the diene system, which makes the sulfur much more basic.

In conclusion, we report herein the first example of an S-coordinated thiophene undergoing reaction. In fact, it appears that the thiophene in **1** is activated to react with "$Fe(CO)_3$" since thiophene itself does not react[18] with $Fe_2(CO)_9$ under conditions very similar to those in eq 1. (Under more vigorous conditions, $Fe_3(CO)_{12}$ reacts with thiophene to give thiaferroles and ferroles.[19]) Thus, it is possible that on an HDS catalyst initial S adsorption of thiophene to a single metal site would activate the diene system to coordinate to a second metal. Perhaps in this bridging position with weakened C–S bonds, the thiophene undergoes C–S bond cleavage and hydrogenation. Investigations of such reactivity are in progress.

Acknowledgment. We thank Dr. L. M. Daniels for help in solving the X-ray crystal structure. The diffractometer was funded in part by the National Science Foundation (Grant No. CHE-8520787).

Supplementary Material Available: ORTEP drawing of **2** and tables of crystal data, positional and thermal parameters, complete bond distances and angles, and least-squares planes for **2** (11 pages); calculated and observed structure factors for **2** (15 pages). Ordering information is given on any current masthead page.

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[12] **2**: IR (hexanes) ν(CO) 2064, 2002, 1988, 1922, 1862 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.95 (m, 2 H, T), 3.56 (m, 2 H, T), 1.98 (s, 15 H, Cp*); ^{13}C NMR ($CDCl_3$) δ 208.5 and 207.0 (CO), 95.5 (C of Cp*), 83.9 and 57.1 (T), 10.5 (C of Cp*); CIMS (methane) *m/e* 603 ($M^+ + H$), 574 ($M^+ - CO$), 546 ($M^+ - 2CO$), 519 ($M^+ + H - 3CO$), 491 ($M^+ + H - 4CO$), 462 ($M^+ - 5CO$). Anal. Calcd for $C_{19}H_{19}O_5FeReS$: C, 37.94; H, 3.18. Found: C, 38.08; H, 3.16.

[13] Crystallographic data for **2**: mol wt 601.47; monoclinic, space group $P2_1/c$ (No. 14); $a = 11.395$ (2) Å, $b = 13.310$ (1) Å, $c = 14.636$ (3) Å, $\beta = 109.151$ (8)°, $V = 2096.8$ (6) Å^3, $\rho_{calcd} = 1.905$ g/cm^3 for $Z = 4$ at 22 ± 1 °C, $\mu = 66.59$ cm^{-1} (Mo Kα). Diffraction data were collected at 22 ± 1 °C using an Enraf-Nonius CAD4 automated diffractometer. A total of 7716 reflections were collected. Of the 3684 unique data, 2850 data were considered observed, having $F_o^2 > 3\sigma(F_o^2)$. An empirical absorption correction was applied to the data based on a series of φ-scans. The positions of the metal atoms were given by direct methods. (SHELXS-86, G. M. Sheldrick, Institut für Anorganische Chemie der Universität, Göttingen, F.R.G.). The remainder of the non-hydrogen atoms were located in difference Fourier maps following least-squares refinement of the known atoms. $R = 0.0263$ and $R_w = 0.0372$.

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[16] Chen, J.; Angelici, R. J. *Organometallics* **1989**, *8*, 2277.

[17] Chen, J.; Daniels, L. M.; Angelici, R. J. *J. Am. Chem. Soc.*, accepted for publication.

[18] Determined by studying the ^1H NMR spectrum of a THF-d_8 solution of $Fe_2(CO)_9$ (10 mg, 0.028 mmol) with thiophene (3.0 μL, 0.037 mmol) at room temperature for 24 h.

[19] Ogilvy, A. E.; Draganjac, M.; Rauchfuss, T. B.; Wilson, S. R. *Organometallics* **1988**, *7*, 1171 and references therein.

Determination of $\delta(^{187}Os)$, $J(Os,X)$, and $T_1(^{187}Os)$ in Osmium Complexes via Indirect 2D NMR Spectroscopy

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Osmium-187 is the most insensitive nucleus in NMR spectroscopy,[1] and also for this reason until now no $\delta(^{187}Os)$ data have been published except for the standard OsO_4[2] and a μ-bridged binuclear complex.[3] Using the indirect two- and one-dimensional (X,Os) NMR spectroscopy (X = ^1H or ^{31}P)[4,5] we have determined to the best of our knowledge for the first time the ^{187}Os chemical shift range, the magnitude and sign of J(Os,X), and $T_1(^{187}Os)$ in quasitetrahedral $[(\eta^5\text{-cyclopentadienyl})(\text{phosphine})_2(R)]Os$ complexes.[6]

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The conventional one-dimensional ^1H and $^{31}P\text{-}\{^1H\}$ spectra of $[(Cp)(phosphine)_2(H)]Os$ show that $^1J(Os,H)$ and $^1J(Os,P)$ are around 70 and 300 Hz, respectively. These scalar coupling constants were used for determination of $\delta(^{187}Os)$ employing the indirect two-dimensional (X,Os) NMR spectroscopy (X = ^1H[4] and ^{31}P[5]) according to sequence 1. In this sequence the information about the osmium chemical shift is coded in the evolution

$$\begin{array}{lll} 90(X)\text{-}\frac{1}{2J(\mathrm{Os,x})}\text{-} & 180(X) & \text{-FID}(X) \\ & 90(\mathrm{Os})\text{-}t_1/2\text{-} \qquad \text{-}t_1/2\text{-}90(\mathrm{Os}) & \end{array} \tag{1}$$

time t_1 and thus in the corresponding 2D contour diagram $\delta(^{187}Os)$ is displayed in F_1 and $\delta(X)$ in F_2 dimension. In the phosphine complexes $[(\eta^5\text{-}Cp)(L^1,L^2)(R)]Os$ where R = Cl (**1**), Br (**2**), I (**3**), CH_3 (**4**), and H (**5**) and $L^1 = L^2 = Ph_3P$ (**a**), $L^1 = Ph_3P$ and $L^2 = Me_3P$ (**b**), and $L^1 = L^2 = Me_3P$ (**c**), the $\delta(^{187}Os)$ values span more than 2500 ppm.[7] The halogen dependence of $\delta(^{187}Os)$ in **1a**–**3a** is normal. Phosphine ligands with higher donor ability (PMe_3 instead of PPh_3) cause a stronger screening of the metal: In the series **2a**, **2b**, and **2c** $\delta(^{187}Os)$ is −3008, −3324, and −3506, respectively. These findings indicate that the osmium shift is to a significant extent determined by the charge density dependence of the nuclear shielding term.

The arrangement of the cross peaks in the two-dimensional (^1H,^{187}Os) and (^{31}P,^{187}Os) diagram yields the relative signs of $J(H,P)$ respective to $J(Os,P)$ and $J(P,H)$ respective to $J(Os,H)$. In **5a** sequence 1 can be applied for X = ^1H and ^{31}P. In the (^1H,^{187}Os) experiment the cross peaks are split by the passive phosphorus coupling. Since the high-frequency ^1H peak correlates with the low-frequency ^{187}Os peak and phosphorus is the unexcited nucleus it is concluded that $^1J(Os,P)$ is of opposite sign to $^2J(H,P)$. The corresponding (^{31}P,^{187}Os) experiment with selective decoupling of the aromatic protons yields that $^1J(Os,H)$ is of opposite sign to $^2J(P,H)$. Overall, it follows that $^1J(Os,P)$ and $^1J(Os,H)$ are positive and $^2J(P,H)$ is negative.

For as wide an application as possible of the indirect 2D NMR recording technique it is essential that it should also work when the scalar couplings are small ($J(Os,X) < 10$ Hz). In **4a** and **4c** ($\delta(^{187}Os) = -4779$) $^2J(Os,H)$ to the methyl protons is 6.0 and 5.4 Hz, respectively. While it is hard to resolve these couplings in a conventional 1D spectrum it is straightforward to determine $^2J(Os,H)$ by sequence 1 either in a 1D [$t_1 = 0$ in (1)] or by an indirect 2D experiment. This may consist of an (^1H,^{187}Os) or a corresponding (^{31}P,^{187}Os) spectrum with CW decoupling of the PPh_3 signals. If both 2D experiments are performed, then it can be shown that the sign of $^3J(P,H)$ is positive and that of $^2J(Os,H)$ negative.

A comparison of the reduced coupling constants $^nK(Os,X) = {}^nJ(Os,X)/h(2\pi/\gamma_{Os})(2\pi/\gamma_X)$ in **1a**–**5a** with those of the homologous iron complexes[5] yields $^1K(Os,P)/^1K(Fe,P) = 7.3$ and in addition for **5a** $^1K(Os,H)/^1K(Fe,H) = 11.5$. These values are in good agreement with the ratio of the s-electron densities at the nucleus of the metals osmium and iron, which lies around 7.4.[8] Thus it can be assumed that $^1J(Os,P)$ and $^1J(Os,H)$ are dominated by the Fermi contact term.

Even under favorable NMR recording conditions the direct determination of $T_1(^{187}Os)$ is extremely difficult. Until now by a special pulse technique only in OsO_4 $T_1(^{187}Os)$ has been estimated to lie between 1 and 26 s at $B_0 = 1.8$ Tesla.[2] If, however, Os has an observable scalar coupling with a more sensitive X nucleus, then not only $\delta(^{187}Os)$ but also $T_1(^{187}Os)$ can be determined with the sensitivity of the X nucleus indirectly by employing

$$\begin{array}{ll} 90(X)\text{-}\frac{1}{2J}\text{-}180(X)\text{-}\frac{1}{2J}\text{-}\Theta(X)\text{-}\frac{1}{2J}\text{-} & \text{-}\frac{1}{2J}\text{-}\Theta(X)\text{-}\frac{1}{2J}\text{-}180(X)\mathrm{FID}(X) \\ 90(\mathrm{Os}) \quad 180(\mathrm{Os}) \quad 90(\mathrm{Os})\text{-}\tau\text{-}90(\mathrm{Os}) & 180(\mathrm{Os}) \quad 90(\mathrm{Os}) \end{array} \tag{2}$$

pulse sequence 2 for X = ^1H[9-11] and ^{31}P. In Figure 1 the results for $[(\eta^5\text{-}Me_5Cp)(cycloocta\text{-}1,5\text{-}diene)(H)]Os$ (**6**) ($\delta(^{187}Os) = -4889$) are presented. In **6** (X = ^1H, Θ = 90°) the intensity of the satellites decays exponentially as a function of τ and this yields $T_1(^{187}Os) = 5.6 \pm 0.6$ s. In **5a** $T_1(^{187}Os)$ is 1.6 ± 0.2 s. Relatively short relaxation times ($0.5 < T_1 < 1$ s) were also obtained for complexes **1a** and **2a**. Here $T_1(^{187}Os)$ was determined via sequence 2 employing X = ^{31}P, Θ = 45°, and proton decoupling.[12] When the PPh_3 ligands are replaced by PMe_3, then $T_1(^{187}Os)$ becomes significantly longer: e.g. in **2c** $T_1(^{187}Os)$ is 6.7 s.

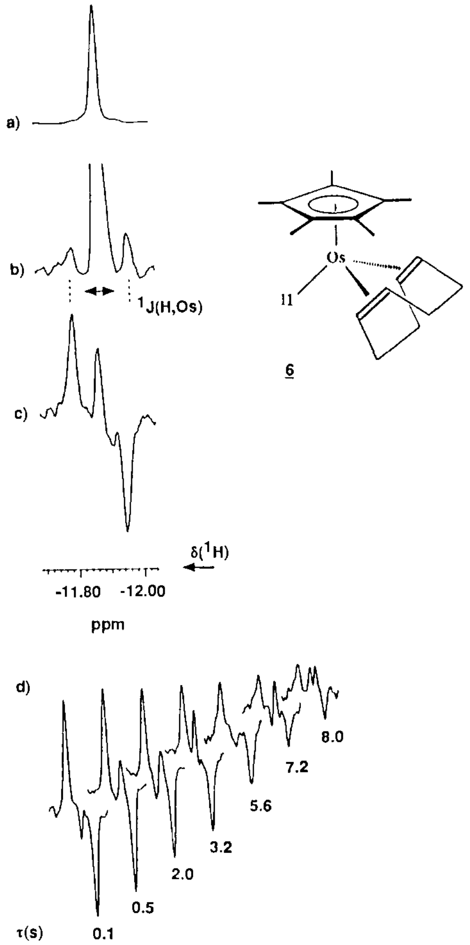

Figure 1. 400.13-MHz ^1H NMR spectrum of **6** in the region of the hydride signal: (a) conventional 1D spectrum, (b) same as (a) but with 32-fold expansion in the vertical, (c) after applying sequence 1 ($t_1 = 0$) and with the satellites in antiphase and suppression of the parent signal, (d) intensity of the satellites as a function of τ.

These results clearly demonstrate that ^{187}Os NMR spectroscopy is a suitable probe for characterization of Os complexes in inorganic and organometallic chemistry. Since in **1**–**6** the longitudinal Os relaxation times lie between 0.5 and 10 s at 9.4 T it appears that in addition to 2D (^1H,^{187}Os) and (^{31}P,^{187}Os) experiments even the indirect 2D (^{13}C,^{187}Os) shift correlation spectroscopy will become attractive for the investigation of com-

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[7] Relative to $\delta(OsO_4) \equiv 0$ $\delta(^{187}Os)$ in **1a** −2595, **2a** −3008, **3a** −3530, **4a** −4411, **5a** −5186 ppm. Typical $T_1(^{31}P)$ values of these complexes are around 1 s.

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[9] Indirect $T_1(^{13}C)$ determination via (2) using enriched samples, cf.: Sklenář, V.; Torchia, D.; Bax, A. *J. Magn. Reson.* **1987**, *73*, 375. Kay, L. E.; Jue, T.; Bangerter, B.; Demou, P. C. *J. Magn. Reson.* **1987**, *73*, 558.

[10] Indirect T_1 (^{13}C) determination via a 2D ^1H NMR pulse sequence using samples with ^{13}C in natural abundance, cf.: Nirmala, N. R.; Wagner, G. *J. Am. Chem. Soc.* **1988**, *110*, 7557.

[11] In all samples measured the concentration was less than 100 mg in 0.5 mL (T = 300 K, B_0 = 9.4 Tesla throughout; some special experimental NMR hardware details for the indirect 2D (X,Y)-$\{^1H\}$ triple resonance spectroscopy are mentioned in ref 5).

[12] The heteronuclear (X,^{187}Os)-$\{^1H\}$ triple resonance scheme described here enables the measurement of $T_1(^{187}Os)$ also via ^{31}P and thus the accuracy of this technique can be checked. In $[(\eta^5\text{-}Cp)(\eta^2\text{-}H_2C{=}CHC_6H_{13})(Ph_3P)(H)]Os$ there are two {Os,X} spin systems and $T_1(^{187}Os)$ was determined indirectly via X = ^1H and ^{31}P. Within the limits of error (∓0.3 s) both experiments yielded $T_1(^{187}Os)$ = 2.2 s. Caution, however, is necessary when the indirect detection scheme according to (2) is applied to $\{Os,X_n\}$ spin systems with $n \neq 1$.[9] In e.g. **5a** $T_1(^{187}Os)$ detected via ^{31}P ($\{Os,P_2\}$) is smaller than 1 s, while 1.6 ∓ 0.2 s was obtained using detection via ^1H ($\{Os,H\}$).

pounds such as Os carbonyl complexes ($^1J(^{187}Os,^{13}CO)$ is around 100 Hz[13]). Moreover, the indirect determination of T_1 via sequence 2 is the method of choice for low-γ spin $^1/_2$ nuclei in natural abundance samples where there is an observable scalar coupling to a sensitive nucleus like ^1H, ^{19}F, or ^{31}P.

Acknowledgment. F.L.O. thanks the Alexander von Humboldt Stiftung for the grant of a stipend.

Registry No. 1a, 79151-48-7; **1b**, 122967-30-0; **1c**, 78251-04-4; **2a**, 34742-23-9; **2b**, 122967-31-1; **2c**, 82675-76-1; **3a**, 80822-03-3; **3b**, 122967-32-2; **3c**, 122967-35-5; **4a**, 122967-29-7; **4b**, 122967-33-3; **4c**, 122967-36-6; **5a**, 80822-04-4; **5b**, 122967-34-4; **5c**, 122967-37-7; **6**, 100603-30-3; ^{187}Os, 15766-52-6.

Supplementary Material Available: Indirect 2D ($^1H,^{187}Os$) and ($^{31}P,^{187}Os$) correlation diagrams of **5a** and **4a**, respectively (2 pages). Ordering information is given on any current masthead page.

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(13) Koridze, A. A.; Kizas, O. A.; Nadezhda, N.; Petrovskii, P. V.; Grishin, Y. K. *J. Chem. Soc., Chem. Commun.* **1981**, 853. Gallop, M. A.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc., Chem. Commun.* **1987**, 1831.

Acid Catalysis of the Photochemical Deconjugation Reaction of 3-Alkyl-2-cyclohexenones[1]

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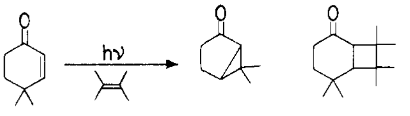
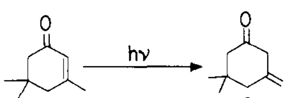
The most common photochemical reactions of simple 2-cyclohexenones are cycloadditions to alkenes[2] and lumiketone rearrangement[3] (eq 1); in addition, if a methyl group is present



(1)

in the 3-position, then photochemical rearrangement to the exocyclic deconjugated isomer can occur[4] (e.g., **1** → **2** in eq 2). The



1 2

(2)

deconjugation reaction is also seen for cyclohexenones which are part of fused ring systems.[4c,5] Despite extensive examination, many aspects of the mechanisms of these photochemical reactions remain controversial. In particular, the details of the mechanism of the deconjugation reaction are confused. For example, it has been reported that photochemical deconjugation unaccountably fails for the corresponding 3-ethyl- and 3-isopropyl-2-cyclohexenones,[4b] and there are conflicting results which suggest that the reaction is[5d,f] or is not[5m] second order in enone. The reaction is also oddly solvent sensitive and, depending upon the cyclohexenone structure, usually[4c,d,5d,g,h,j,l] but not always[5a–c,e] fails in alcohols, usually[4c,5g,i,j] but not always[5i] proceeds in alkane solvents, is relatively efficient in benzene[4c,5c–e,h,j,l] and ethyl acetate,[4d,5l] and proceeds in acetonitrile[4c] but not ether.[5i]

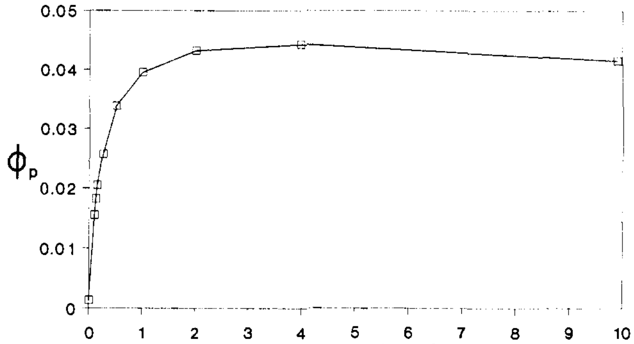


Figure 1. Photochemical isophorone deconjugation at various concentrations of acetic acid: [isophorone] = 0.145 M.

We report here our finding that the photochemical deconjugation reaction of 3-alkylcyclohexenones requires the presence of small amounts of weak acid in order to proceed and that many of the unusual features of the reaction are explained by a mechanism involving acid catalysis.

The quantum yield of deconjugation measured when benzene solutions of 3,5,5-trimethyl-2-cyclohexenone (isophorone, eq 2) were irradiated[6] was found to be variable and apparently depended upon the state of purity of the isophorone. Somewhat unexpectedly, the quantum yield declined when increasingly pure samples of isophorone were used. Addition of small amounts of acetic acid increased the quantum yield beyond that obtained with the least pure samples of isophorone, and a limiting upper value of efficiency was reached at approximately 4 × 10^{-3} M acid (Figure 1).[7] This suggests that an acidic impurity is present in crude samples of isophorone and that this impurity is required for deconjugation to occur. The presence of such an impurity may account for the earlier finding[5d,h] that the deconjugation of some enones is apparently second order in enone since increasing the concentration of the enone would increase the concentration of the impurity responsible for enhancing the efficiency of deconjugation. Similarly, the reported efficiency of the deconjugation reaction for isophorone in ethyl acetate[4d] may reflect the presence of low levels of acetic acid in this solvent.

Quenching of the deconjugation reaction with isoprene gave a linear Stern–Volmer plot with no curvature at high quencher concentrations. This suggests the involvement of a single excited state; the $k_q\tau$ value was 60 which implicates the lowest triplet excited state of isophorone in the reaction assuming typical values of cyclohexenone triplet lifetimes and rate constants for triplet quenching.[8]

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(1) Contribution No. 422 from the Photochemistry Unit, University of Western Ontario.

(2) Weedon, A. C. In *Synthetic Organic Photochemistry*; Horspool, W. M., Ed.; Plenum: New York, 1984; pp 61–143.

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