the triplet state takes place before reaction with the aromatic nucleus.

Reactions were carried out between $MeSO_2N_3$ and methyl benzoate or benzotrifluoride in the presence of suitable additives in the hope of catalyzing the singlet → triplet conversion and then observing the pattern of substitution expected from the latter species. Some of the data are given in Table II.[11]

Table II. Methanesulfonamidation of Methyl Benzoate and Benzotrifluoride in the Presence of Various Additives

Conditions	% products				
	ortho	*meta*	*para*	$MeSO_2$-NHC_6-H_4X	$MeSO_2$-NH_2
	a. $PhCO_2Me$				
Sealed tubes under N_2	64.3	34.4	1.3	21.4	4.6
With oxygen	55.1	42.6	2.3	20.5	5.3
CCl_4 (40 molar excess)	62.9	35.0	2.1	12.9	*a*
CH_2Br_2 (40 molar excess)	29.9	57.5	12.6	1.1	44.2
Cobalt(III) acetylacetonate	32.3	63.3	4.4	2.2	*a*
Manganese(II) acetylacetonate	27.3	68.2	4.5	1.3	*a*
Manganese(II) acetylacetonate (trace)	61.4	37.1	1.5	16.6	*a*
$MnCl_2 \cdot 4H_2O$	61.6	36.7	1.67	13.6	*a*
Gattermann copper	56.2	40.5	3.3	5.8	*a*
Iron powder	60.7	37.9	1.4	19.1	*a*
	b. $PhCF_3$				
Degassed under N_2	53.4	45.6	1.0	20.4	21.9
With oxygen	48.0	47.5	4.5	24.4	16.0
CH_2Br_2 (20 molar excess)	34.3	50.0	15.7	0.94	46.5
Copper(II) acetylacetonate	38.2	58.1	3.7	4.3	29.5
Manganese(II) acetylacetonate	43.9	54.1	2.0	4.1	29.0
$Co_2(CO)_8$	31.2	66.8	2.0	2.9	16.1
$Fe_3(CO)_{12}$	30.7	64.0	5.3	0.75	61.5
$Fe(CO)_5$	23.8	69.7	6.5	0.55	53.2

[a] Not determined.

Though there is considerable scatter of results among the different reaction conditions they appear to be generally consistent with a trapping by the additive (or side-tracking to an intermediate that abstracts hydrogen), efficient to varying degrees, of the triplet species present or formed, so that the pattern of substitution is more characteristic of an attack by a singlet species the more efficient the trapping becomes. With methylene bromide present in excess the main product was that of hydrogen abstraction (presumably by triplet nitrene) from CH_2Br_2 and the yield of substitution product dropped considerably. The proportion of *para* isomer formed was, exceptionally, also greater than in other cases, but the *meta* isomer predominated, as predicted on the basis of an addition by singlet nitrene. Carbon tetrachloride appeared ineffective. Transition metal compounds had a similar effect to CH_2Br_2, but to different extents depending on the nature of the addendum and its concentration. Manganous chloride, copper, and iron (all insoluble in the medium) had little, if any, influence upon the isomer ratio. The results are thus consistent with the intervention of both singlet and triplet sulfonyl nitrenes in these media.

Acknowledgments. The initial part of this work was supported by a National Research Council of Canada grant, and more recent aspects by a National Science Foundation grant (GP-8869), both of which are gratefully acknowledged.

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(11) All new compounds were adequately characterized.

(12) To whom inquiries should be addressed at the University of Alabama.

R. A. Abramovitch,[12] G. N. Knaus, V. Uma
Departments of Chemistry
University of Saskatchewan, Saskatoon, Canada
and University of Alabama, University, Alabama 35486

Received August 8, 1969

Intermolecular Energy Transfer and Sensitized Photolysis in the Biacetyl–Tetrachloroplatinate(II) System

Sir:

Sensitized photolysis has been a very useful tool for the analysis of the photochemical fates of organic molecules. Very recently, studies have begun to show that the technique can be extended to the study of inorganic complexes in solution. In 1968, Vogler and Adamson reported on the biacetyl–Co(III) ammine system,[1] and in 1969, Porter discussed the biacetyl–cobalticyanide system.[2] Other observations have demonstrated quenching of organic triplets by coordination compounds.[3–7]

We wish to report the results on the sensitized photoaquation of tetrachloroplatinum(II) complex. The observed absorption bands of $PtCl_4^{2-}$ at 330, 390, 470, and 550 mμ correspond to the transitions $^1A_{1g} \rightarrow {}^1E_g$, $^1A_{1g} \rightarrow {}^1A_{2g}$, $^1A_{1g} \rightarrow {}^3A_{2g}$, and $^1A_{1g} \rightarrow {}^3E_g$, respectively, in agreement with the assignment of Basch and Gray.[8] The high-energy triplet ($^1A_{1g} \rightarrow {}^3B_{1g}$) reported[9] to occur at 417 mμ could not be observed since it is masked by the adjacent intense singlet ($^1A_{1g} \rightarrow {}^1A_{2g}$) transition. The triplet transition ($^1A_{1g} \rightarrow {}^3E_g$) was seen as a shoulder. It has not been observed in solution before.

The singlet transition of biacetyl occurs at 405 mμ, but is much less intense than the singlet transitions of $PtCl_4^{2-}$. Although the singlet–singlet transitions of biacetyl and $PtCl_4^{2-}$ overlap, it is possible to use a large excess of biacetyl and an almost negligible amount of the complex, such that most of the excitation energy is absorbed by biacetyl (donor).

A thoroughly degassed solution of 0.5 *M* biacetyl was excited with stimulating light from a 200-W xenon lamp and the emission spectrum recorded (Aminco-Bowman spectrofluorimeter) is given in Figure 1. Fluorescence occurs at 470 mμ and phosphorescence at 523 mμ with a ratio of 1:1.7. The phosphorescence of biacetyl is completely quenched in presence of 1×10^{-3} *M* $PtCl_4^{2-}$, while the fluorescence intensity remains essentially unchanged (Figure 1). Oxygen has a similar quenching effect on the phosphorescence of biacetyl and

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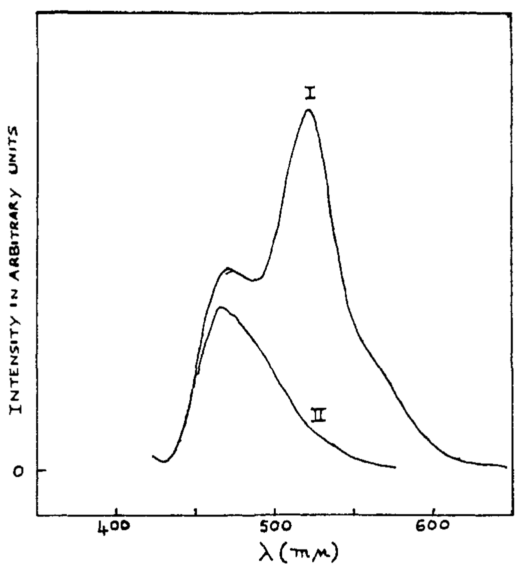

Figure 1. (I) Emission spectrum of 0.1 *M* biacetyl in aqueous solution. (II) Emission spectrum of 0.1 *M* biacetyl and 0.001 *M* $PtCl_4^{2-}$. Excitation at 405 mμ.

is more effective than $PtCl_4^{2-}$ (not shown in Figure 1). $PtCl_4^{2-}$ by itself did not show any luminescence. Thus the results of emission studies lead us to postulate triplet–triplet energy transfer from biacetyl to $PtCl_4^{2-}$. The quenching rate constant for the biacetyl–$PtCl_4^{2-}$ system calculated from the emission spectra (Figure 1) is about $3 \times 10^7\ M^{-1}sec^{-1}$, which is considerably less than diffusion-controlled rates.

$PtCl_4^{2-}$ is known to undergo photoaquation with a quantum yield of 0.14 at 313, 404, and 472 mμ, and 0.65 at 254 mμ.[10] Photolysis of $PtCl_4^{2-}$ with 404-mμ radiation from a 1000-W xenon–mercury lamp yields $[PtCl_3 \cdot H_2O]^-$. The final spectrum of $[PtCl_3 \cdot H_2O]^-$ obtained by thermal equilibration of $PtCl_4^{2-}$ was found to be in complete agreement with the spectrum reported in the literature.[11]

Some quantitative measurements of the quantum yield for the photoaquation of $PtCl_4^{2-}$ both in the presence and in the absence of biacetyl as sensitizers have been made. With irradiation at 404 mμ and 0.034 *M* $PtCl_4^{2-}$ and 0.001 *M* $HClO_4$, a quantum yield of 0.16 ± 0.02 was obtained, which is in good agreement with the value of 0.14 reported in the literature.[10] A solution 0.5 *M* in biacetyl, 0.005 *M* in $PtCl_4^{2-}$, and 0.001 *M* in $HClO_4$ gave a value of 0.26 ± 0.02 with 404-mμ radiation, using reineckate[12] and ferrioxalate[13] actinometry. Balzani and Carassiti[10] interpreted the constancy of the quantum yield of 0.14 at 313, 404, and 472 mμ as due to a complete deactivation of the ligand field singlets (313, 404 mμ) and the triplet (472 mμ) to the lowest triplet (555 mμ) state, which could be the common precursor of the photoaquation having a quantum yield of 0.14. On the basis of our results on quantum yields the following scheme is proposed.

$$(\text{biacetyl})_{S_0} \xrightarrow{h\nu} (\text{biacetyl})_{S_1}$$

$$(\text{biacetyl})_{S_1} \longrightarrow (\text{biacetyl})_{T}$$

$$(\text{biacetyl})_{T} \longrightarrow (\text{biacetyl})_{S_0} + h\nu^1 \text{ (phosphorescence)}$$

$$(\text{biacetyl})_{T} + (\text{complex})_{S_0} \longrightarrow (\text{complex})_{T}\ (^1A_{1g} \longrightarrow {}^3E_g)$$

$$(\text{complex})_{T} \longrightarrow \text{product}$$

The higher yield of the sensitized reaction suggests the important result that the unsensitized reaction does not proceed by complete conversion of all higher excited states to the lowest triplet. In fact, since we report here a total yield for sensitized and direct reaction, it is true that the actual sensitized yield is larger than 0.26, and it may well be true that the quantum yield from the lowest triplet of the Pt complex is quite close to unity.

Acknowledgment. We thank the National Research Council (Canada) for support.

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V. S. Sastri, C. H. Langford[14]
Department of Chemistry, Carleton University
Ottawa 1, Canada

Received October 1, 1969

Photolytic and Catalytic Decomposition of an α,α'-Bisdiazo Ketone. A Cyclopropenone Pathway

Sir:

Recent investigations into the photolysis[1,2] and silver oxide catalyzed decomposition[3] of α,α'-bisdiazocyclohexanones have resulted in isolation of the corresponding ring-contracted α,β-unsaturated acid or ester in yields ranging from 18 to 60% as the only characterized products. In each case, the products have been rationalized as having been formed *via* a Wolff rearrangement followed by a hydrogen migration, with no consideration given to the possibility of a cyclopropenone intermediate.

To study this possibility, the synthesis of 1,3-bisdiazo-1,3-diphenyl-2-propanone (**1**) was undertaken in the hope of isolating diphenylcyclopropenone. By the dropwise addition of *p*-toluenesulfonyl azide[4] to a solution of dibenzyl ketone and sodium ethoxide in ethanol at 0° followed by addition of water, orange solid was obtained and recrystallized in small amounts by dissolving in hexane at room temperature and cooling to −20° to give a 44% yield of **1**,[5] mp 93° dec. The spectral data were in agreement with the proposed structure:[6] ir (CCl_4) 2090, 2040, 2035 cm^{-1} ($C{=}N_2$), 1630 cm^{-1} ($C{=}O$); nmr $(CCl_4)^7$ τ 2.65 (broad singlet); uv (hexane) λ_{max} 264 mμ (ε 23,500), 324 (ε 7100); uv (methanol) λ_{max} 264 (ε 21,000), 328 (ε 10,100).

Treatment of **1** with sodium formate in concentrated formic acid and sodium acetate in glacial acetic acid

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