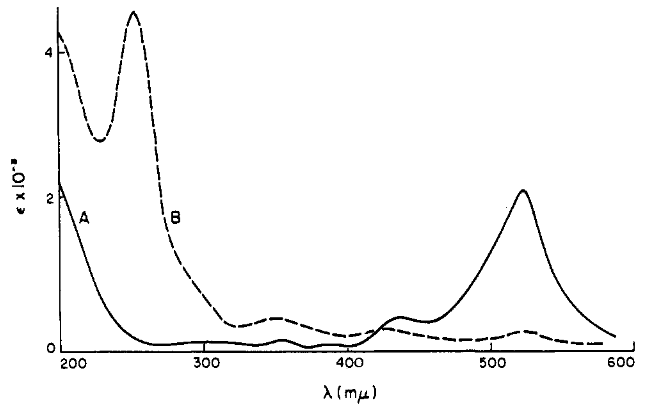

Figure 1.

for Se_4^{2+}. Curve B was obtained from a 2:1 Te:$S_2O_6F_2$ mixture in fluorosulfuric acid and shows an intense absorption at 250 mμ with two weak maxima at 360 and 420 mμ. This spectrum also contains a very weak 510-mμ peak, which we have never been able completely to eliminate from the yellow solutions.

Conductometric and cryoscopic measurements were carried out on red solutions produced by the reaction of tellurium with pure fluorosulfuric acid. Values of γ, the number of fluorosulfate ions produced by one atom of tellurium, were calculated by comparison with the conductivity of potassium fluorosulfate. At both temperatures studied, γ was essentially constant over the concentration range studied and had values of 0.69 ± 0.02 at 25° and 0.72 ± 0.01 at −86.4°. A value of 1.71 for ν, the number of particles produced per atom of tellurium, was obtained from the cryoscopic results.

For the formation of polyatomic cations of general formula Te_n^{x+}, the reaction is

$$n\text{Te} + 2x\text{HSO}_3\text{F} = \text{Te}_n^{x+} + \frac{x}{2}\,\text{SO}_2 + \frac{x}{2}\,\text{HF} + \frac{x}{2}\,\text{H}_3\text{O}^+ + \frac{3x}{2}\,\text{SO}_3\text{F}^- \quad (1)$$

The equilibrium

$$\text{H}_3\text{O}^+ + \text{SO}_3\text{F}^- \rightleftarrows \text{HF} + \text{H}_2\text{SO}_4 \quad (2)$$

would affect the value of γ, but not the value of ν which would be $(1 + 3x)/n$. The equilibrium constant, K, for reaction 2 has the values 0.12 at 25°, 0.042 at 0°, and 0.031 at −78°.[3] The value at −86.4° has not been measured but in view of the above figures a value of 0.030 is reasonable. The relation between γ and the values of x and n is complicated, but it can be shown that

$$\gamma = \frac{x}{n}\{(K - 3.50) + (K^2 + 5K + 0.25)^{1/2}\}(2K - 2)^{-1}$$

Using the above values of K, $\gamma = 1.39x/n$ at 25° and $\gamma = 1.47x/n$ at −86.4°. The experimental γ values give $x/n = 0.495 \pm 0.015$ at 25° and 0.497 ± 0.007 at −86.4°. At both temperatures it is thus clear that $n = 2x$, and the red species contains tellurium in the $+{}^1/_2$ oxidation state. This corresponds to species such as Te_2^+, Te_4^{2+}, Te_6^{3+}, etc. The expected values of ν for the various species are shown below.

Ion:	Te_2^+	Te_4^{2+}	Te_6^{3+}	Te_8^{4+}	Te_{10}^{5+}
γ	2.00	1.75	1.67	1.62	1.60

The observed value of 1.71 agrees best with the formation of Te_4^{2+} or Te_6^{3+}. Measurement of the magnetic susceptibility of a concentrated red solution of tellurium in fluorosulfuric acid showed the solute to be diamagnetic with a susceptibility of -27×10^{-6} cgs units per g-atom of Te. Thus the species Te_6^{3+} can be ruled out as it would be expected to be paramagnetic.

The Raman spectrum of the red solution in fluorosulfuric acid showed two peaks which can be attributed to tellurium–tellurium bonds: a very strong peak at 219 cm⁻¹ and a very weak peak at 139 cm⁻¹. This spectrum is very similar to that of Se_4^{2+} which has a strong band at 327 cm⁻¹ and a very weak band at 188 cm⁻¹.[4] An as yet incomplete X-ray crystallographic investigation of the Se_4^{2+} cation in the compound $Se_4(HS_2O_7)_2$ has shown that Se_4^{2+} very probably has a square-planar structure.[5] The infrared and Raman spectra are also consistent with this structure. In view of the similarities between the absorption spectra and the Raman spectra of Te_4^{2+} and Se_4^{2+}, we propose a similar square-planar structure for Te_4^{2+}.

The reaction of tellurium with antimony pentafluoride gives rise to several compounds which are not easy to separate. There is certainly, however, a red compound containing the Te_4^{2+} cation and a yellow compound which appears to have the composition $TeSbF_6$ and in which tellurium is probably present in the +1 oxidation state. This appears to be the oxidation state of tellurium in the yellow solutions of tellurium in acid solvents. Our investigation of the nature of this species is not yet complete.

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Energy-Transfer Reactions of $N_2(A^3\Sigma_u^+)$I. Quenching and Emission by C_2N_2, SO_2, and Other Molecules

Sir:

In a previous paper[1] we described the production of a flow of metastable $N_2(A^3\Sigma_u^+;\ v' = 0, 1)$ molecules[2] in a mixture of argon and nitrogen at 1–5 torr pressure in the absence of other reactive species. This was confirmed by detection of the nitrogen (A–X) Vegard–Kaplan (V–K) bands in emission and by energy-transfer reactions with Hg, NO, and CO giving ($^3P_1$), ($A^2\Sigma^+$), and ($a^3\Pi$) emission, respectively. With the argon–nitrogen flow system we have now studied the reactions of $N_2[A^3\Sigma_u^+;\ v' = 0$ (142 kcal), 1 (146 kcal)] with oxygen, nitrous oxide, ethene, benzene, iodine, acetophenone, biacetyl, carbon disulfide, cyanogen, and sulfur dioxide. These reactions apparently proceed by collisional quenching with energy transfer from $N_2(A)$, and it appears that $N_2(A)$ can serve as a triplet sensitizer for the 142–146-kcal mole⁻¹ energy region which is at present inaccessible.[3]

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The four molecules, O_2, N_2O, C_2H_4, and C_6H_6, all rapidly quench the V–K emission without apparently giving rise to subsequent emission. The available energy of N_2(A) is sufficient to dissociate O_2 or N_2O by

$$N_2(^3\Sigma_u{}^+) + O_2(^3\Sigma) \longrightarrow N_2(^1\Sigma_g{}^+) + 2O(^3P) \quad (\Delta H^\circ = -23 \text{ kcal mole}^{-1})$$

$$N_2(^3\Sigma_u{}^+) + N_2O(^1A) \longrightarrow 2N_2(^1\Sigma_g{}^+) + O(^3P) \quad (\Delta H^\circ = -102 \text{ kcal mole}^{-1})$$

The latter reaction has been suggested on the basis of O-atom formation in active nitrogen systems,[4] and our observations confirm that such reactions may occur. Ethene and benzene have available both triplet and singlet states. The absence of emission may arise from inadequate detection for the highly forbidden triplet–singlet transitions, or from possible dissociation or quenching of the excited states.

The addition of iodine to N_2(A) showed a weak emission which consisted of only the "continuum" between 2500 and 3450 Å, maximum at 3425 Å. Our observation confirms the suggestion that this emission previously observed in active nitrogen was excited by N_2(A),[5] and lends support to the proposal that the excited state[6] is a triplet ($^3\Sigma_u{}^-$). Phillips[5a] suggests that the iodine 4300-Å continuum is also excited by reaction between ground-state I_2 and N_2(A). This is not confirmed by our study and must derive from some other energy carrier in his active N_2 system.

Acetophenone and biacetyl were used because the phosphorescence spectra of their lowest triplet states are known.[3] These molecules quenched the V–K bands and gave a pale greenish-looking emission which was just detectable with our monochromator–photomultiplier arrangement. The emission spectra were similar to the known phosphorescence spectra of the lowest triplet states at 73.6 and 54.9 kcal.[3] It is interesting that these molecules can accept as much as 142 kcal of energy in an upper triplet level and internally convert to the lowest triplet without significant dissociation at pressures of ~2 torr.

Cyanogen, sulfur dioxide, and carbon disulfide all have known triplet levels,[7] and we hoped to observe emission directly from these levels. In each case the addition to the N_2(A) flow quenched the V–K emission and gave emissions which will be discussed separately.

The low-resolution emission spectrum from C_2N_2 is shown in Figure 1. This is the $\tilde{a}\,^3\Sigma_u{}^+$–$\tilde{X}\,^1\Sigma_g{}^+$ transition;[7,8] the progressions in the v_1'' frequency are the most prominent. These band heads were accurately identified by recording the emission photographically (Jarrell–Ash 0.75-m spectrograph, 12-hr exposure at 100-μ slits). The intense heads of this system are clearly doubled on the photographs with a splitting of 18 ± 4 cm^{-1}. This splitting corresponds to the absorption spectrum[7] and arises from transitions in which 1 quantum of v_5 is excited in both electronic states. The predicted splitting on this basis is 22 cm^{-1}. The full analysis of the weaker bands of Figure 1 will be presented later. This is the first time the C_2N_2($^3\Sigma_u{}^+$–$^1\Sigma_g{}^+$) system has been observed in emission in the gas phase. The emission has previously been observed only in inert gas matrices.[9] In one instance,[9a] active nitrogen was used as the excitation source, and it was suggested that the N_2($A\,^3\Sigma_u{}^+$) was responsible. We confirm this for the gas phase with our apparatus. We also have tentative evidence that the C_2N_2 may be partially dissociated to CN radicals. These observations are relevant for eventually understanding the gas-phase reactions of active nitrogen with cyanogen.[10]

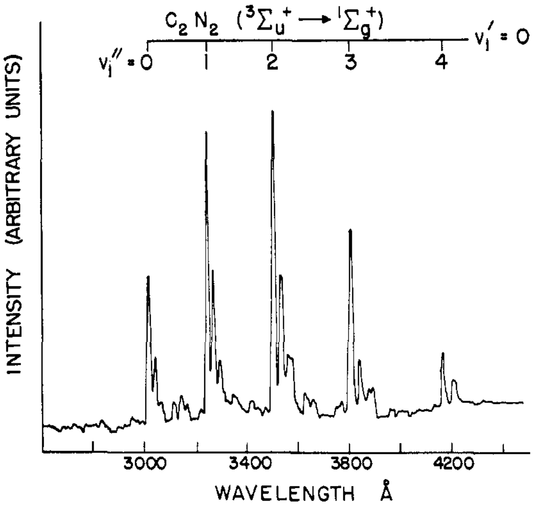

Figure 1. Low-resolution photoelectric scan of the emission spectrum from N_2($A\,^3\Sigma_u{}^+$) + C_2N_2 at 2 torr (Jarrell–Ash 0.75-m Czerny–Turner monochromator, EMI 9558Q phototube, PAR phase lock amplifier).

The addition of SO_2 to N_2(A) gives a vibrationally relaxed triplet emission ($\tilde{a}\,^3B_1$–$\tilde{X}\,^1A_1$) similar to that observed by Gaydon[11] and Thrush.[12,13] Starting at 2500 Å, singlet emission ($\tilde{A}\,^1B_1$–$\tilde{X}\,^1A_1$),[13,14] apparently continuous, was also observed. The intensity ratio of triplet to singlet emission (I_t/I_s) is pressure dependent, increasing by a factor of 2 from 0.5 to 5 torr. A possible mechanism includes an intersystem crossing from highly excited triplet to the fluorescent singlet state. The reverse collisionally induced case SO_2($^1\tilde{B}_1$) → SO_2($^3\tilde{B}_1$) has been suggested in various studies.[12,13,15] Conflicts[12,15,16] in the literature for values of SO_2 rate constants prevent definite analysis of our data.

The addition of CS_2 to N_2(A) gave a greenish flame which consists of a continuum extending from 3500 to 6000 Å with maxima at 4500 and 5400 Å separated by a

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minimum at 5100 Å. This emission may correspond to the known absorption system ($\tilde{a}^3A_2$–$\tilde{X}^1\Sigma_g^+$),[6,17] but higher intensity and higher resolution spectra are required before this can be definitely proven.

This paper shows the usefulness of our flow system for studying the reactions of $N_2(A^3\Sigma_u^+)$ in the absence of other reactive species. This interesting metastable is important for understanding the chemistry of active nitrogen[5b] and also promises to be a good sensitizing agent for study of high-energy triplet states.

Acknowledgment. This work was supported by the Research Grants Branch, National Center for Air Pollution Control, Bureau of Disease Prevention and Environmental Control, under Contract AP-00391.

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(19) Alfred P. Sloan Foundation Fellow.

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Catalysis of Addition of Deuterium to Ethylene over Zinc Oxide

Sir:

Addition of deuterium to ethylene is catalyzed by a variety of solids. With transition metals[1] the product (with light ethylene as a reactant) is a mixture represented by the formula $C_2H_{6-x}D_x$ ($0 \leq x \leq 6$), and the yield of $C_2H_4D_2$ is usually less than 50%. Oxides also catalyze hydrogenation reactions.[2] In one case, chromia,[3] it has been shown that addition of deuterium to ethylene yields about 99% $C_2H_4D_2$. Recently, we have found that zinc oxide also catalyzes the addition of deuterium to ethylene with $C_2H_4D_2$ yields of approximately 99%.

Two samples of zinc oxide were used in this work. Sample I was prepared by heating zinc oxalate in oxygen at 500° for 16 hr. Sample II was Kadox-25, a product of the New Jersey Zinc Co. In the standard pretreatment, the catalyst was degassed for 4 hr at 450°, reduced with dried hydrogen at 350° for 40 min, and degassed at 400° for 3 hr.

Analyses of the products by mass spectroscopic techniques are shown in Table I, along with comparable data for a chromia catalyst prepared by the procedure suggested by Burwell.[3] Essentially pure dideuterioethane is formed. Comparison of the fragmentation pattern of the product with that of authentic samples of CH_2DCH_2D and CH_3CHD_2 show that the ethane product is more than 95% 1,2-dideuterioethane.

Table I. Product Distribution

	Product %		
Sample (temp, °C)	C_2H_6	C_2H_5D	$C_2H_4D_2$
ZnO-I (60)	0.0	2.0	97.5
ZnO-II (25)	0.0	0.1	99.9
Cr_2O_3 (−78)	0.0	0.0	100.0

Most of our studies have centered on the zinc oxide II. In a circulating system with a volume of 100 cc, the half-time for ethylene conversion ($H_2:C_2H_4$ = 130 mm:13 mm) is 15 min at room temperature. Even at −78° conversion is readily observable, *i.e.*, about 20%/hr. Comparison with activities per square meter for ethylene hydrogenation over zinc oxide reported by other workers[4,5] are listed in Table II. It seems clear that this catalyst (prepared by burning zinc in air) is significantly more active than those prepared by decomposition of the hydroxide[4] or oxalate.[5,6]

Table II. Comparison of Activities over ZnO

Ref	Activity,[a] molecules cm^{-2} sec^{-1}	Order H_2	Activation energy, kcal
This work	3.3×10^{11}	0.5	~10
4	2.5×10^{6}	1	22.4
5	1.2×10^{10}	~0	22.4

[a] Computed at 298 and 100 mm of hydrogen.

It has been suggested[2] that the pattern of activity for transition metal oxides can be correlated to the configuration of the d electrons. Clearly, this is not the case with zinc oxide. Indeed, the similarity of zinc oxide and chromia oxide with regard to selectivity suggests the possibility that the selective ethylene hydrogenation activity occurs on similar sites. Since unfilled d shells are not a *sine qua non* for activity, these sites may be anion vacancies.[7] If, on such isolated sites, only one carbon surface bond can be formed, it seems reasonable to suppose[3] that ethyl radicals form irreversibly by an insertion reaction of ethylene into a hydrogen-covered site. Such a pathway would explain the selectivity. Furthermore, if these are the sites of catalytic activity on oxides, all active oxides in contrast to metals should show selective 1,2 addition of deuterium to ethylene at moderate temperatures.[8]

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

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(7) The "strained" sites of S. W. Weller and S. E. Voltz, *ibid.*, 76, 4695 (1954), may be interpreted as surface anion vacancies.
(8) NOTE ADDED IN PROOF. Dr. Atsumu Ozaki of Tokyo Institute of Technology has informed me that addition of deuterium to ethylene over Co_3O_4 also leads to $C_2H_4D_2$ with C_2H_6.

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