entirely upon exact molecular eigenstates and recognizes the differences in energy levels between cis and trans isomers of the same molecule. We have emphasized the importance, for experimental demonstration of this cis/trans control, of a number of molecular features reiterated below.

Specifically, one must be able to produce a *single excited molecular eigenstate* which spans the full conformational space of the molecule, i.e., a state above or close to the top of the barrier to isomerization in the excited electronic state. This necessitates that any barrier in the excited state be low enough that the vibronic state density permits the excitation of a single energy eigenstate. Further, in order to be able to influence the product ratio for the isomerization reaction, there must be relatively isolated transitions to states of the desired conformation. These conditions were not met by the first example in section 4.3 but the second example, where the molecular features were more favorable, showed considerable control over the cis/trans ratio.

The conditions on the molecular parameters go hand-in-hand with those that must be imposed on the exciting and down pumping lasers, the power and duration of which must be such that "clean" transitions are pumped and the pumping must occur at a rate faster than that for spontaneous emission.

To simplify the computations we have considered a model with only vibrational motion. Including rotations is necessary, of course, in any analysis of a real molecular system. However, the essential principles outlined in this paper are unaltered by including rotations. The principal effect of incorporating rotations would be to increase the state density, necessitating use of longer pulses to isolate individual states.

This paper also contains extensive calculations on two versions of a model which were designed to examine features of polyatomic molecules which are of importance to the feasibility of laser-induced isomerization. Case 1, for example, showed extensive interleaving of cis and trans transitions so that effective control is difficult to achieve. This was not the situation for case 2 which has a smaller difference in the cis and trans equilibrium energies and which allows for extensive trans-cis induced isomerization. Thus, we anticipate that laser-induced isomerization will be experimentally demonstrable for molecules with level structures similar to those of case 2.

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Registry No. trans-Stilbene, 103-30-0; cis-stilbene, 645-49-8.

A High-Temperature Photochemistry Study of the Reaction between Ground-State Cu Atoms and N₂O from 470 to 1340 K

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The Metals-HTP (high-temperature photochemistry) technique has been adapted for studies with thermally unstable reactants, here N₂O. The rate coefficients for the reaction Cu(4s ${}^{2}S_{1/2}$) + N₂O \rightarrow CuO + N₂ from 470 to 1190 K are best fitted by $k_1(T) = 1.7 \times 10^{-10} \exp(-5129 \text{ K/T}) \text{ cm}^3$ molecule⁻¹ s⁻¹ with 2 σ precision limits varying from ±8 to ±18%, depending on temperature, and corresponding 2 σ accuracy limits of ±22 to ±27%. It is shown that this expression correlates well with data on a series of other metal atom-N₂O reactions. Above about 1190 K, the Arrhenius plot shows distinct upward curvature, which may be due to a contribution to the observed rates of vibrationally excited N₂O in bending modes. For the entire 470–1340 K range the measurements are best described by $k_1(T) = 3.04 \times 10^{-20} T^{2.97} \exp(-3087 \text{ K/T}) \text{ cm}^3$ molecule⁻¹ s⁻¹ with estimated 2 σ accuracy limits of ±22 to ±28%.

1. Introduction

Recently, we reported on the development of the Metals-HTP (high-temperature photochemistry) technique,¹ to complement our well-established HTFFR (high-temperature fast-flow reactor) method for studying reactions of metallic and other refractory species. Metals-HTP differs from regular HTP^{2,3} in that metal salts are evaporated in the apparatus to replace permanent gases as atom precursors. In HTP techniques, atoms are produced photolytically and the reactions are observed in real time in the same volume element in which they are formed; pressures that can be utilized range from about 40 mbar to around atmospheric, and wall reactions are negligible. In HTFFR experiments, atoms

or radicals are produced upstream of the reaction zone by evaporative 4,5 or microwave 6 methods and pressures are typically in the 5-80 mbar range.

In the first Metals-HTP study we made measurements on the termolecular $Na + O_2 + N_2 \rightarrow NaO_2 + N_2$ reaction. Here we report on the first bimolecular reaction studied by this technique

$$\operatorname{Cu}(4s \, {}^{2}\mathrm{S}_{1/2}) + \mathrm{N}_{2}\mathrm{O} \rightarrow \mathrm{CuO} + \mathrm{N}_{2} \tag{1}$$

No previous studies on this reaction have been reported, but more metal atom oxidation reactions with N_2O have been studied than with any other oxidant, (see e.g. ref 4 and section 3), which allows

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Figure 1. Schematic of the modified Metals-HTP reactor used for part of this study.

observation of trends in rate coefficients and activation energies (section 3).

2. Technique

2.1. Experiment. Cu atom resonance fluorescence was used to measure the rates of reaction 1. The initial experiments were carried out in the previously described¹ reactor. N₂O was found to inhibit vaporization; hence, the oxidant was introduced downstream of the vaporizer at a distance z, from the N₂O inlet to the center of the reaction zone, of 24.5 cm. For experiments above about 900 K, with the thermally unstable reactant N_2O , a number of modifications were necessary; see Figure 1. Most importantly, a cooled N₂O inlet was added, similar in design to those used in regular HTP studies. This caused the vaporizer to be moved from the center of the 5.0-cm-diameter reaction tube to a position ≈ 1 cm from the alumina wall. The vaporizer consisted of an alumina or boron nitride crucible, contained in a molybdenum coil and heated by the reaction tube walls. The vaporizer position was adjusted to obtain a desirable rate of vaporization. Typically, the tip of the crucible was 12-19.5 cm upstream of the observed reaction zone. To reduce the scattered light background, a 0.6-cm-diameter, 5-cm-length collimating tube was placed in the side arm in front of the photomultiplier tube (PMT) and the side arm on the opposite port was removed. The heating performance was improved by installing larger 1.25-cmdiameter SiC heating rods. Cu atoms were generated from vaporized Cu_2Cl_2 or CuF_2 by excimer laser photolysis at 248 nm. In a few experiments, 193 nm was used instead; see Table I. The laser was operated at 2 Hz. Laser energy was varied using neutral density filters made from overlapping metal gauzes. The laser energy was determined by measuring the percentage transmission of each filter, using a calibrated Gentec power meter. A Cu hollow-cathode lamp provided the 324.7-nm resonance radiation. This radiation was focused into a 1-cm-diameter beam at the center of the reaction zone using a quartz lens of 20-cm focal length. Quartz windows were used on the reactor ports on both the laser and hollow-cathode lamp sides.

The resonance fluorescence intensity is monitored by the PMT after passing through a Pyrex window and a 327 ± 16 or 324.7 ± 2.5 nm (fwhm) interference filter; compare Table I. The PMT signal was fed through an EG&G PAR 1121-A amplifier-discriminator to a Nicolet LAS 12/70 multichannel scaler (MCS), operated with 256 time channels. Signals from 300 to 1000 laser pulses were averaged to construct temporal profiles of the Cu atom fluorescence intensity (Figure 2). The data were then transferred to an IBM personal computer for data reduction. In some experiments the PMT signal was instead fed to an EG&G ORTEC MCS card, in the IBM PC, through a preamplifier.

The temperature of the reaction zone was measured before and after each experiment with a retractable Pt/Pt-13% Rh ther-



Figure 2. An example of a temporal profile of Cu atom fluorescence intensity, fit to an exponential decay, eq 4 at T = 528 K, $[O_2] = 8.16 \times 10^{15}$ molecules cm⁻³, and $[Ar] = 7.7 \times 10^{17}$ molecules cm⁻³, to yield $k_{ps1} = 191.2 \pm 6.1$ s⁻¹.



Figure 3. A typical plot of the pseudo-first-order rate coefficient k_{ps1} versus [N₂O] at T = 1068 K and [Ar] = 1.68×10^{18} molecules cm⁻³ to yield $k_1 = 1.06 \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹.

mocouple, doubly shielded to minimize radiation effects. Temperature drift in the course of an experiment was typically less than 10 K. Flow rates of all gases were determined using calibrated mass flow meters and mass flow controllers. Pressures were measured with an FPI pressure transducer. The reactor gases used were 99.998% Ar from liquid Ar (Linde), atomic absorption grade N₂O (99.0%, Linde), and 0.53% N₂O (99.99%) in Ar (99.999%, Matheson). The photolytes used were Cu₂Cl₂ (ACS reagent grade, Baker) and CuF₂ (99%+, Aldrich).

2.2. Data Handling. Measurements in the HTP reactor are made under pseudo-first-order conditions, ¹⁻³ i.e., [Cu] \ll [N₂O]. The decrease of [Cu] after the photolysis pulse is given by

$$-d[Cu]/dt = \{k_1[N_2O] + k_D\}[Cu]$$
(2)

$$= k_{\rm ps1}[\rm Cu] \tag{3}$$

where k_1 is the rate coefficient at any T and P, k_D represents Cu atom loss, essentially by diffusion, and k_{ps1} is the pseudo-first-order rate coefficient. Fluorescence intensity I, at time t after photolysis, is proportional to [Cu]. Thus, from eq 2, I is given by

$$I = I_0 \exp(-k_{\rm ps1}t) + B \tag{4}$$

where I_0 is the fluorescence intensity immediately following the laser pulse and *B* is the background intensity. The nonlinear least-squares fitting routine, used to determine $k_{ps1} \bullet \sigma_{kps1}$ from the temporal profile of the Cu atom fluorescence intensity (Figure 2), has been described in detail previously.⁷ Typically, five k_{ps1} values are obtained using different [N₂O], while keeping *T* and *P* constant. $k \bullet \sigma_k$ is evaluated by plotting $k_{ps1} \pm \sigma_{kps1}$ against [N₂O] (Figure 3), the error analysis for which is the same as

TABLE I:	Summary	of	the	Rate	Coefficient	Measurements	for	Cu	+	$N_2($)
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		[] [] []					
<i>T</i> , K	P, mbar	[M], 10 ¹⁸ cm ⁻³	$[N_2O]_{max},$ 10 ¹⁴ cm ⁻³	<i>z</i> , cm	\bar{v} , cm s ⁻¹	LE, mJ	$k \pm \sigma_k,$ cm ³ molecule ⁻¹ s ⁻¹
471ª	55	0.85	256	24.5	22	180 (0) ^b	$4.00 \pm 0.15 \ (-15)^c$
473	101	1.57	595	24.5	20	255 (0)	$2.83 \pm 0.12 (-15)$
476ª	114	2.30	350	24.5	29	150 (0) ^d	$2.78 \pm 0.24 (-15)$
479ª	65	0.99	528	24.5	26	185 (0)	$3.62 \pm 0.35 (-15)$
494	44	0.65	370	24.5	17	255 (0)	6.33 ± 0.13 (-15)
4984	57	0.83	189	24.5	22	230 (0)	$9.48 \pm 0.51 (-15)$
578	50	0.82	269	24.5	22	255 (0)	835 ± 0.48 (-15)
520	61	0.84	694	24.5	10	250 (0)	$6.55 \pm 0.54 (-15)$
5524	124	1 76	269	24.5	19	225 (0)	$1.07 \pm 0.07 (-14)$
555	1 J 4 55	1.70	1202	24.5	27	223 (0)	$1.07 \pm 0.07 (-14)$ 1.07 $\pm 0.33 (-14)$
5555- 5580	23 74	1.74	04 2	24.3	27	230 (0)	$1.97 \pm 0.33 (-14)$
554-	/0	0.65	7 4 .3 191	24.J DA 5	20	125 (0)d	$2.00 \pm 0.10 (-14)$
555	42	0.33	201	24.3	1/	135 (0)-	$1.00 \pm 0.10 (-14)$
337"	/3	0.99	100	24.5	20	40 (3)	$2.43 \pm 0.10 (-14)$
203	103	1.55	47.0	24.5	23	210 (0)	$1.23 \pm 0.10 (-14)$
590"	50	0.62	119	24.5	27	225 (0)	$2.70 \pm 0.13 (-14)$
593	103	1.27	197	24.5	21	15 (4)	$3.11 \pm 0.24 (-14)$
6194	64	0.75	90.5	24.5	20	225 (0)	$6.00 \pm 0.04 (-14)$
620	56	0.65	108	24.5	19	275 (0)	$3.80 \pm 0.20 (-14)$
623	134	1.56	103	24.5	26	260 (0)	$2.78 \pm 0.12 (-14)$
648	70	0.78	49.1	24.5	24	210 (0)	$5.48 \pm 0.26 (-14)$
656	70	0.77	72.4	24.5	13	210 (0)	$6.50 \pm 0.30 (-14)$
665	96	1.04	70.4	24.5	16	$15 (3)^{d}$	$9.52 \pm 0.81 (-14)$
665	96	1.04	70.4	24.5	16	30 (2) ^d	7.82 ± 0.59 (-14)
672	60	0.65	58.1	24.5	25	50 (2)	$7.85 \pm 0.30 (-14)$
703	69	0.71	36.3	24.5	27	200 (0)	$1.18 \pm 0.06 (-13)$
705	96	0.98	27.7	24.5	9	200 (0)	$1.80 \pm 0.18 (-13)$
737ª	90	0.89	35.6	24.5	22	160 (0)	$1.11 \pm 0.15 (-13)$
807	178	1.60	28.5	24.5	35	260 (0)	$1.84 \pm 0.08 (-13)$
829	81	0.71	28.0	24.5	31	280 (0)	$3.00 \pm 0.23 (-13)$
842	73	0.63	7.62	8.5	17	350 (0)	$5.35 \pm 0.40 (-13)$
843ª	230	1.98	5.39	5.0°	17	225 (0)	$2.71 \pm 0.15 (-13)$
858	146	1.23	19.7	24.5	31	15 (4)	$4.46 \pm 0.16 (-13)$
860	72	0.61	22.4	24.5	27	50 (2)	$5.99 \pm 0.24 (-13)$
8754	69	0.57	6 38	10.0	23	195 (0)	6.35 ± 0.17 (-13)
8854	98	0.81	17.0	24.5	42	120 (0)	$4.61 \pm 0.25 (-13)$
888	227	1 86	18.2	24.5	31	10 (4)	$3.89 \pm 0.24 (-13)$
800	87	0.71	7.61	8 50	19	350 (0)	6.22 ± 0.24 (13)
Q114	277	2 00	4 75	5.00	16	180 (0)	651 ± 0.41 (-13)
Q1Q ^a	140	1 10	3 80	10.0	25	180 (0)	9.38 ± 0.54 (-13)
0724	191	1 34	3 40	5.04	25	230 (0)	7.38 ± 0.29 (-13)
0204	244	1.57	3.47	10.0	20	200 (0)	$1.10 \pm 0.04 (-12)$
10024	140	1.04	2.07	5.04	22	180 (0)	$1.10 \pm 0.04 (-12)$ 1.13 $\pm 0.09 (-12)$
10404	204	2.04	2.32	10.04	20	160 (0)	$1.13 \pm 0.09 (-12)$ 1.27 ± 0.09 (-12)
1042"	270	2.00	J.74 7 AA	5 00	23		$1.37 \pm 0.07 (-12)$ 1.06 ± 0.02 (-12)
10034	247	1.00	2.44 A 10	5.0° 10.0¢	23	170 (0)	$1.00 \pm 0.03 (-12)$ $1.03 \pm 0.08 (-13)$
1093"	249	2.30	4.19	10.0	21	170 (0)	$1.93 \pm 0.08 (-12)$
1098"	239	1.70	3.03	3.0	22	223 (0)	$1.33 \pm 0.04 (-12)$
11024.7	191	1.27	2.49	12.0	18	290 (0)	$1.43 \pm 0.09 (-12)$
1115	124	0.81	1.07	0.U ^e	27	2/5 (0)	$1.53 \pm 0.03 (-12)$
1132"	354	2.27	2.29	5.0*	19	125 (0)	$1.81 \pm 0.03 (-12)$
1168"	284	1.76	2.06	10.0*	19	165 (0)	$2.09 \pm 0.24 (-12)$
1178", j	199	1.23	1.29	6.0 ^e	18	340 (0)	$3.39 \pm 0.12 (-12)$
11884,5	126	0.78	1.08	12.0	29	290 (0)	$2.38 \pm 0.14 (-12)$
1192"	239	1.45	2.03	5.0°	28	210 (0)	$1.70 \pm 0.15 (-12)$
1245 ^{<i>a</i>, <i>j</i>}	198	1.15	1.06	6.0 ^e	25	340 (0)	$4.86 \pm 0.20 (-12)$
1249 ^{<i>a</i>, <i>j</i>}	126	0.73	0.99	12.0 ^e	31	275 (0)	$3.46 \pm 0.21 (-12)$
12794.5	170	0.97	0.88	9.0 ^e	30	340 (0)	$4.55 \pm 0.18 (-12)$
1298 ^{<i>a</i>, <i>f</i>}	326	1.82	0.94	9.0 ^e	16	300 (0)	$5.18 \pm 0.12 (-12)$
1298 ^{<i>a</i>, <i>f</i>}	252	1.41	1.20	6.0 ^e	20	340 (0)	$6.21 \pm 0.20 (-12)$
1320 ^{<i>a</i>, <i>f</i>}	223	1.23	0.87	9.0 ^e	23	320 (0)	6.64 ± 0.33 (-12)
1339 ^{a, f}	331	1.81	1.20	4.0 ^e	12	290 (0)	$7.66 \pm 0.24 (-12)$

^{*a*}CuF₂ photolyte was used instead of Cu₂Cl₂. ^{*b*}The number in parentheses indicates the number of neutral density filters used. ⁽⁵Should read as $(4.00 \pm 0.15) \times 10^{-15}$ cm³ molecule⁻¹ s⁻¹. ^{*d*}193-nm laser photolysis was used instead of 248-nm photolysis. ⁽⁵The reactor of Figure 1 was used with 0.53% N₂O in Ar; in all other experiments the reactor of ref 1 with pure N₂O was used. $^{f}324.7 \pm 2.5$ nm filter used instead of 327 ± 16 nm filter.

discussed before.^{8,9} In evaluating the k(T) expression, σ_T/T , as in previous work, 1 is taken to be 2%.

In earlier HTP studies, a single value χ_v^2 was used as a measure of goodness of the fits like those of Figure 2.^{1,7,8} Here residual analysis, a stricter test that reveals systematic deviations from the exponentiality over the entire reaction time scale, is employed.¹⁰

Since the method is described in detail elsewhere,¹¹ only the essential features are briefly mentioned here. First the residual, a measure of the scatter of the data about the fit, RES_i , is plotted against t_i , the time at which point *i* is recorded. RES_i is defined as

$$RES_i = I_i - [I_0 \exp(-k_{ps1} t_i) + B]$$
(5)

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For a good fit, visual inspection of the residual plot should show points scattered evenly about zero throughout the reaction time scale. Next a run test is made. This takes into account the number of runs in the residual plot. A run is a continuous series of residuals of the same sign. The probability of obtaining the observed number of runs, compared to that of a normal probability distribution, is then computed from

$$Z = (u - \mu + 0.5) / \sigma$$
 (6)

where Z is the unit normal variate for the observed u runs, and μ and σ are the mean and standard deviation of the normal distribution calculated for the particular set of data.¹⁰ If very small probabilities ($\leq 20\%$) are obtained for a series of fluorescence profiles, the experiment should be discarded; however, this situation has not been encountered in this work.

To ensure the validity of the k(T) expressions, a residual analysis is again made. Here the residual, normalized with respect to temperature

$$\operatorname{RES}(T_i) = (k(T_i) - k_{\operatorname{fit}}(T_i)) / k_{\operatorname{fit}}(T_i)$$
(7)

is analyzed for randomness against the independent variable $1/T_i$ and against the parameters [M], LE, \bar{v} , and z/\bar{v} discussed in the next section.

3. Results and Discussion

The 470-1340 K temperature range was found to be suitable for the present measurements. The lower limit was determined by the heating required for the vaporization of the photolytes and the upper limit by the thermal stability of N_2O . Use of higher temperatures led to a sharp decrease in the observed rate coefficients. This upper limit compares favorably to the about 950 K limit for N₂O studies in HTFFRs where wall decomposition of this compound is apparently significant.^{12,13}

The k_1 measurements are summarized in Table I. The results are seen to be independent of [M], varied over the $(0.55-2.3) \times$ 10^{18} molecule cm⁻³ range, and of the average gas velocity \bar{v} , changed from 9 to 42 cm s⁻¹. The inlet to reaction zone distance, z, which was adjusted from 5 to 24.5 cm, was selected such as to assure that mixing was at least 95% complete.¹⁴ $k_1(T)$ may be seen to show no consistent variation with z either, nor with z/\bar{v} , the residence time for mixing prior to photolysis (0.18-2.7 s). Thus, it may be concluded that the gases were well mixed, thermal equilibrium was attained, and there was no significant thermal dissociation of N_2O . Furthermore, the results are seen to be independent of laser energy LE, varied from 10 to 350 mJ, and the photolyte used $(Cu_2Cl_2 \text{ or } CuF_2)$. This implies that the measured rate coefficients were independent of the initial [Cu] and that there were no kinetic complications from processes involving photolysis or from reaction products. The data are also seen to be independent of the method of vaporization of the precursors and the N2O supply used. However, when 193-nm laser photolysis was used, an analysis of the residual plots showed that the decay profile of the Cu atom fluorescence intensity was found to fit eq 4 poorly. Photolyte concentration had to be kept very low to ensure a good fit. Hence, only a few results were obtained using 193-nm laser photolysis (Table I). No such problems were encountered with 248-nm laser radiation, which was therefore used in most of this work. Within the scatter of the data no curvature is evident in the Arrhenius plot until about 1190 K. Hence, an Arrhenius expression $k(T) = A \exp(-B K/T)$ can be used to fit those data (Figure 4). The corresponding best-fit expression obtained using the Marquardt algorithm from Bevington¹⁵ is

 $k_1(T) = 1.70 \times 10^{-10} \exp(-5129 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (8)

Sciences; McGraw-Hill: New York, 1981; Chapter 11.



Figure 4. Plot of the measured rate coefficients for the $Cu + N_2O$ reaction, showing best fits: (O) measured rate coefficients; (-) best fit to data from T = 470 K to T = 1190 K, eq 8; (...) best fit to data from T = 470 K to T = 1340 K, eq 9.

with variances and covariances $\sigma_A^2 = 1.7 \times 10^{-2} \text{ A}^2$, $\sigma_B^2 = 1.0 \times 10^4$, and $\sigma_{AB} = 1.2 \times 10^1 \text{ A}$. These values are combined using the method of Wentworth¹⁶ to calculate 2σ precision limits, which are at a minimum of $\pm 8\%$ at 850 K and increase to a maximum of $\pm 18\%$ at 470 K. Allowing for possible systematic errors of $\pm 20\%$, the overall 2σ accuracy limits are estimated to vary from ± 22 to $\pm 27\%$. We recommend this expression also for extrapolation to temperatures below 470 K. However, for temperatures above 1190 K, upward curvature is seen in Figure 4. An expression of the form $k(T) = AT^n \exp(-E K/T)$ fits all 470–1340 K data well and yields the empirical fit

$$k_1(T) =$$

3.04 × 10⁻²⁰(T/K)^{2.97} exp(-3087 K/T) cm³ molecule⁻¹ s⁻¹
(9)

with variances and covariances $\sigma_A^2 = 1.89 \times 10^1 \text{ A}^2$, $\sigma_n^2 = 3.14 \times 10^{-1}$, $\sigma_E^2 = 1.95 \times 10^5$, $\sigma_{An} = -2.44 \text{ A}$, $\sigma_{nB} = -2.42 \times 10^2$, and $\sigma_{AB} = 1.89 \times 10^3 \text{ A}$. The resulting 2σ precision limits are at their their second seco minimum of $\pm 8\%$ at 1000 K and reach a maximum of $\pm 20\%$ at 470 K with corresponding 2σ accuracy limits of ± 22 to $\pm 28\%$.

It should be noted that the curvature suggested by $(T/K)^{2.97}$ in eq 9 exceeds that which could be predicted from transition-state theory.¹⁷ Plane^{18,19} has observed pronounced upward curvature in the Arrhenius plots of Li and K atom-N₂O reactions above about 600 K, which he attributed there to the participation of N_2O in bending vibrational modes in the reactions. In the bent geometry the vertical electron affinity of N₂O is sufficiently large that an ionic/covalent curve crossing can occur at close range in those reactions giving rise to channels with enhanced rate coefficients.¹⁸ Because of the much larger ionization potential of Cu (745 kJ mol⁻¹ versus 520 and 419 kJ mol⁻¹ for Li and K, respectively), such a curve crossing cannot occur for $Cu + N_2O_1$, as was determined using an ionic model²⁰ which takes into account the attractive Coulombic and polarization potentials and the repulsive Born potential. However, the reaction of Cu with N₂O in bending modes can lead to an activated complex with enhanced resonance stabilization. The enhancement occurs because of the larger electron affinity of bent N_2O ; this is explicitly visible by

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Figure 5. Plot of experimental 300 K rate coefficients of metal atom-N₂O reactions against ionization potential plus s-p promotion energy. The data are from Table II.

using the resonance model of ref 20. The barrier is then suppressed, thereby producing a faster reaction channel at elevated temperatures, where higher populations of N₂O in bending modes exist. Another factor that could lead to enhanced rate coefficients at elevated temperatures is the A coefficient of this reaction, which is expected to be larger because of the greater electron affinity of bent N₂O.²¹

While no previous data for the reaction between ground-state Cu and N_2O have been reported, a large number of rate coefficient measurements of metal atom $-N_2O$ reactions are available. It is interesting to see whether there are correlations between those rate coefficients and whether the Cu data in that sense agree with these earlier observations. Since most measurements were made at 300 K, we compare the rate coefficients at that temperature and extrapolate the other data to that temperature. This also allows excluding consideration of the uncertain contribution of vibrationally excited N₂O in some of the reactions. We thus find that there is a close fit between these rate coefficients and the sum of the ionization potential of the metal atom and the energy PE required to promote an s electron to the lowest vacant p orbital, i.e., the s-p hybridization energy. Both these factors are taken into account as the metal atom has both partial ionic and partial sp hybrid bonding character in the activated complex. This correlation is shown in Figure 5, based on the input data of Table II, for alkaline earth and transition metals, as well as Cu. The rate coefficient values are those from isolated elementary reaction measurements. In another paper²⁰ we show that this correlation can be explained on the basis of resonance theory and reflects in fact a trend of activation barriers E, as defined by $k(T) = AT^n$ exp(-E/RT). It is also found that similar but separate tight fits

TABLE II: Summary of Input Data and Measurements on Metal Atom-N₂O Reactions Used for Figure 5

metal	<i>T</i> ,ª K	IP, ^b kJ mol ⁻¹	PE, ^c kJ mol ⁻¹	$k(300 \text{ K}), \text{ cm}^3$ molecule ⁻¹ s ⁻¹
Mg	450-900	738	419	$2.8 \times 10^{-18 d}$
Ca	250-900	590	181	1.4×10^{-12e}
Ba	300900	503	147	3.1×10^{-11f}
Sc	300	631	187	$1.1 \times 10^{-12} g$
Ti	300	658	190	$4.2 \times 10^{-13 g}$
v	300	651	196	$4.7 \times 10^{-13 g}$
Cr	298	653	279	$1.0 \times 10^{-14 h}$
Fe	296	762 ⁱ	231	≤2.0 × 10 ^{-15 j}
Mo	1200-3100	684 [*]	306	$3.4 \times 10^{-15} m$
Cu	470-1190	745	365	$6.4 \times 10^{-18 n}$

^a For reactions measured at several temperatures above 300 K only, the temperature range is that over which the Arrhenius fit is linear; e.g., for Cu we used eq 8 and estimated the k(300 K) value by extrapolating it down to 300 K. ^b Unless otherwise indicated, the values are obtained from the ionization potentials in: Moore, C. E. Ionization Potentials and Ionization Limits Derived from the Analysis of Optical Spectra. Natl. Stand. Ref. Data Ser., Natl. Bur. Stand. (U.S.) 1970, 34. ^cFrom: Moore, C. E. Atomic Energy Levels as Derived from the Analyses of optical Spectra. Natl. Bur. Stand. (U.S.), Circ. 467, Vol. I (1949) through Vol. III (1958). ^d Private communication from J. M. C. Plane. ^e Plane, J. M. C.; Nien, C. J. Phys. Chem. 1990, 94, 5255. ^fNien, C.; Plane, J. M. C. J. Chem. Phys. 1991, 94, 7193. ^gRitter, D.; Weisshaar, J. C. J. Phys. Chem. 1990, 94, 4907. h Parnis, J. M.; Mitchell, S. A.; Hackett, P. A. J. Phys. Chem. 1990, 94, 8152. ¹Worden, E. F.; Comaskey, B.; Densberger, J.; Christensen, J.; McAfee, J. M.; Paisner, J. A. J. Opt. Soc. Am. B 1984, 1, 314. ^JMitchell, S. A.; Hackett, P. A. J. Chem. Phys. 1990, 93, 7822. * Rayner, D. M.; Mitchell, S. A.; Bourne, O. L.; Hackett, P. A. J. Opt. Soc. Am. B 1987, 4, 900. MAkhmadov, U. S.; Zaslonko, I. S.; Smirnov, V. N. Kinet. Catal. 1988, 29, 808. "Present study.

can be obtained for the N₂O reactions with the alkali metals and with B, Al, and Ga. The latter correlates with the ionization potential plus the sp²-hybridization energy. The rate coefficient for the Zn + N₂O reaction²² has not been included in Figure 5 because the value obtained falls several orders of magnitude above what that correlation predicts. This may be due to the fact that in that work "the reactor was operated near the lower limit of the useful range" for that type of apparatus.²² We therefore suggest that that work determined an upper limit to the rate coefficient of Zn + N₂O at 298 K.

In summary, the kinetics of the $Cu + N_2O$ reaction has been obtained over a wide temperature range. The measured rate coefficients, when extrapolated to 300 K, correlate well with those measured in several laboratories for other ground-state metal atoms.

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