## Gaseous reactions and luminescence initiated by triboelectricity

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Mercury shaken at room temperature in the presence of reduced pressure of a hydrocarbon,  $CO_2$ , acetone,  $N_2-H_2$  mixture, etc., induces visible fluorescence and chemical transformations in the gaseous material.

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The appearance of electrification upon rubbing together dissimilar substances is a familiar phenomenon, which is commonly referred to as frictional electrification or triboelectrification.<sup>1</sup> The source of this electrification is the separation of electrical charges caused by contact potential differences. The friction serves merely to bring about intimate surface contact; polished disks of steel and glass when pressed firmly together and then separated show charge separation. This type of charging between metal and glass also occurs when the metal is liquid such as mercury. In this case rubbing is not necessary, mere contact is capable of generating static charges (1).

Triboelectrification is frequently accompanied by optical phenomena, called triboluminescence. Triboelectrification and triboluminescence of solids, in particular, have been widely investigated. The companion triboluminescence of the triboelectrification of liquid mercury – glass system, however, has received attention only in the past decade (2-6) in spite of its discovery centuries ago (7, 8), and apparently no previous study has been reported on the chemistry of gaseous triboelectrical discharges. We have recently initiated a study of these phenomena, in which two particular aspects were explored: visual observation of optical phenomena and a survey of chemical reactions.

The luminescences were produced in a similar fashion as described by earlier workers (6, 7). Evacuated glass ampules were filled with a few Torr of gas material and sealed. The ampules were shaken manually or in a small laboratory vibrator. Luminescence occurs on relative motion of the mercury to the glass as the electrons trapped on unfilled surface sites of the glass jump back to the positively charged mercury pool (6). The effect on the visible emission of the nature of the filling gas, its pressure, temperature, the nature of the wall material and its surface conditions modified by subjecting it to various treatments prior to use were investigated.

Four tube materials, Pyrex glass, Vycor #7910, fused quartz, and plexiglass were examined. They all proved to be effective to produce light. The following gases were investigated: Ne (intense orange-red); He, Ar, Kr, Xe, H<sub>2</sub>, CH<sub>4</sub>, biacetyl, C<sub>2</sub>H<sub>4</sub>, air, Hg (no gas added) (light blue); CO (greenish-blue); N<sub>2</sub> (violet blue).

The use of sodium amalgam instead of pure mercury had the effect of changing the color and suppressing the intensity of emission. A Wood's alloy (Bi, Pb, Sn, and Cd, 50; 26.7; 13.3; 10.0) melting at 70 °C with neon gave the same characteristic orange-red color as with mercury.

The intensity of emission could be increased by increasing the area of contact surface through the use of glass spirals in the tube. The lamp constructed in this manner was suitable for the slow photolysis of acetone vapor.

Earlier spectroscopic studies (2, 5) have shown the presence of He and Ar lines in the luminescence spectra of He and Ar filled luminescence tubes. In order to produce emission from He an excitation energy in excess of 20 eV is required. This suggests that in reactive systems chemical reactions should occur. To investigate the chemistry of these systems, procedures were followed that were similar to those in the luminescence studies. Pyrex vessels (50-100 cc) containing a few grams of mercury were filled with methane (10-50 Torr) and sealed under vacuum. Shaking of the tube in a small laboratory shaker (1-10 h) led to extensive decompositions. The products are listed in Table 1 with yields expressed in relative gas chromatogram peak areas. The most interesting product is  $(CH_3)_2$ Hg, formed in moderately high yields. Some other examples of gaseous reactions are also listed in

<sup>&</sup>lt;sup>1</sup>From the Greek word tribos, which means rubbing.

NOTES

TABLE 1 Product yields from the triboelectrical discharge decomposition of hydrocarbons and acetone\*

Substrate	Pressure (Torr)	Relative gas chromatogram peak areas of products										
		Me₂Hg	$C_2H_2$	$C_2H_4$	C <sub>2</sub> H <sub>6</sub>	H <sub>2</sub>	C <sub>3</sub> H <sub>8</sub>	C <sub>3</sub> H <sub>6</sub>	CH <sub>4</sub>	C₄†	MeHgEt	СО
CH	10	128	60	52	45	29	17	2				
C <sub>4</sub> H <sub>8</sub>	ĩõ	55	60	32	112	12		50	145	35	11	
ČH <sub>3</sub> ČOCH <sub>3</sub>	12	621	_	_	137		23	27	107	45		814
$C_2 H_4$	11	171	2014		208	62	72	147	333		191	_
$\left\{ \begin{array}{l} H_2 \\ C_2 H_4 \end{array} \right.$	8.3 6.6	40	396		130	_	42	21		17	<u> </u>	-

\*Conversions ranged from 5 to 30%. †C<sub>4</sub>-hydrocarbons.

the table, of which the synthesis of ammonia and hydrazine from a 3:1 mixture of  $N_2$  and  $H_2$  is noteworthy.

Similar reactions could be brought about by bubbling the appropriate gases through a pool of mercury.

The mechanisms of these reactions are obviously complex. The processes include electrical breakdown and direct and sensitized photolysis.

These phenomena have implications for gas phase kinetic studies. It is possible to produce spurious reactions in the Toepler pump and in other equipment where moving mercury surfaces are in contact with glass or gas materials. This possibility was checked and from hydrocarbons and acetone, we would indeed produce noncondensable gases on extensive pumping.

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## Kinetics of the exchange reaction of dimethylarsenic deuteride with diethylarsine

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The exchange reaction  $(CH_3)_2AsD + (C_2H_5)_2AsH \Rightarrow (CH_3)_2AsH + (C_2H_5)_2AsD$  can be monitored by conventional nuclear magnetic resonance spectroscopy. The equilibrium constant in diethyl ether- $d_{10}$  solution is 1.2 ± 0.1 and the rate constant for the forward reaction is 4.95 ± 0.25 × 10<sup>-5</sup> 1 mole<sup>-1</sup> s<sup>-1</sup> at 35°. Dimethylarsine exchanges rapidly with methanol- $d_4$  and bis(trifluoromethyl)arsinic deuteride.

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Knowledge of the rate of exchange of secondary arsine protons, as in reaction 1, was important in determining the mechanism of the addition of secondary arsines to hexafluorobutyne-2,

[1] 
$$(CH_3)_2AsD + (C_2H_5)_2AsH \frac{k_1}{k_{-1}} (CH_3)_2AsH + (C_2H_5)_2AsD$$

because the distribution of the deuterium label in

the products of the competitive reaction described by reaction 2, would give mechanistic information

$$\begin{array}{c} (CH_3)_2A_{SD} \\ \hline \\ (C_2H_5)_2A_{SH} \end{array} \\ + CF_3C \equiv CCF_3 \rightarrow \\ (C_2H_5)_2A_SC(CF_3) = C(CF_3) \begin{pmatrix} D \\ H \end{pmatrix} \\ \hline \\ (C_2H_5)_2A_SC(CF_3) = C(CF_3) \begin{pmatrix} D \\ H \end{pmatrix} \\ \hline \\ \end{array}$$